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A Theoretical Study of the Structure and Stability of $H^+(CO)_n$, $H^+(N_2)_n$, and $H^+(O_2)_n$ Clusters (n = 1–6)

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Abstract: An ab initio MO calculation is made for $H^+(CO)_n$, $H^+(N_2)_n$ (n = 1–6), and $H^+(O_2)_n$ (n = 1–4) clusters by using the 4-31G basis set. $H^+(CO)_2$ and $H^+(N_2)_2$, for which linear structures are stable, form shells for clustering reactions. Then, CO and N_2 attack successively the π^*-type MO's of these shells to form clusters up to n = 6. The correlation effect on the stabilization energy of $H^+(CO)_2$ and $H^+(N_2)_2$ is examined with CI of single and double excitations. A general picture of the gas-phase clustering process is discussed on the basis of various theoretical results.

The stability of gas-phase complexes between a proton and a variety of bases (B's) has been examined extensively with the pulsed electron-beam mass spectrometer.[2] Recent experiments revealed the existence of $H^+(B)_n$ complexes (B = N_2, CO, and O_2) and provided their thermochemical data ($\Delta G^\circ_{n-1,n}$, $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$) in the clustering process.[3] It was shown that the stability of H^+B_2 toward the dissociation $H^+B + B$ increases in the order CO < N_2 < O_2, whereas the proton affinity is of the order $O_2 < N_2 <$ CO. For N_2 and CO, the stability of $H^+(B)_n$ decreases very slowly for n = 3–6, but it becomes sharply small at n = 7. For O_2, the observed largest cluster is $H^+(O_2)_4$. These experimental results may be related to the structure and the electronic distribution of the cluster and it is tempting to compare $\Delta H^\circ_{n-1,n}$ with the theoretical data ($\Delta E_{n-1,n}$) to elucidate the clustering mechanism.

In this work, an ab initio MO–CI calculation is made for $H^+(CO)_n$, $H^+(N_2)_n$ (n = 1–6), and $H^+(O_2)_n$ (n = 1–4), and their structures are determined. Also, a general picture of the clustering is discussed on the basis of various theoretical studies.

Method of Calculation

The electronic distribution of $H^+(CO)_n$ and $H^+(N_2)_n$ is calculated by the Hartree–Fock (HF)-SCF method with the 4-31G basis set. The STO-3G basis set was reported to have failed in reproducing the experimental data.[3] Although the 4-31G basis set employed here is small in the sense of accurate energetics, we are obligated to use it owing to the large size of the system. For instance, $H^+(CO)_6$ has 110 functions in this basis set. GAUSSIAN 127 program package[4] which was developed by the Institute for Molecular Science (IMS) is used for the MO calculation. The geometries of $H^+(CO)_n$ and $H^+(N_2)_n$ (n = 1–6) are optimized to minimize the total energies (E_T's), and the stabilization energies ($\Delta E_{n-1,n}$) are evaluated for these series of clusters. To estimate the correlation effect on the stabilization energy, we make CI calculations for $H^+(CO)_2$ and $H^+(N_2)_2$. The CI includes the singly and doubly excited configurations except those from inner (K) shells on the basis of the HF MO. The optimal geometries of $H^+(O)_2$ (n = 1–4) with the nonsinglet spin states are predicted by the unrestricted HF calculations. For the singlet state of H^+O_2 and $H^+(O_2)_2$, the restricted closed-shell wave function is adopted.

HF Results and Discussion of $H^+(CO)_n$, $H^+(N_2)_n$, and $H^+(O_2)_n$

Figure 1, a and b, depicts the optimized structures of $H^+(CO)_n$ and $H^+(N_2)_n$. Table IA gives the energetics of $H^+(CO)_n$ clusters and Table IB is for $H^+(N_2)_n$. Since the trend of the structural changes in both clustering reactions is similar, the reaction of $H^+(CO)_{n-1} + CO \rightarrow H^+(CO)_n$ is examined. When CO is protonated, the length of the new C–H bond of H^+CO is found to be similar to that in the standard hydrocarbons. The proton attacks the σ lone-pair electrons on C to form a strong bond. However, when the second C–O approaches H^+CO, its H–C bond becomes elongated (1.08 → 1.38 Å) in $H^+(CO)_2$. That is, the proton is shared by two CO's in the collinear form, and the H· · ·C bond is weakened. While the structures of H^+CO and $H^+(CO)_2$ are predictable even before the MO calculation and indeed were already investigated with the STO-3G basis set[3] those of larger clusters (n > 2) are hard to predict and are of theoretical interest. The most likely and the highest symmetry structure of $H^+(CO)_3$ is of the equilateral form (D_{3h}). However, its optimized geometry is found to give a positive $\Delta E_{2,3}$ (18.8 kcal/mol, unstable) relative to the infinite separation between $H^+(CO)_2$ and CO (Table IA). Now, we have to seek another geometry of $H^+(CO)_3$ with negative $\Delta E_{2,3}$. As a result of optimization, a T-shaped structure is most stable. It is regarded as a weakly interacting system of $H^+(CO)_2$· · ·CO, where the geometry of $H^+(CO)_2$ is almost maintained for n = 2 → 3. Figure 2, the dominant charge-transfer interactions which determine the shape of the clusters are schematically sketched. Thus we may expect that the further clustering of CO is merely a perturbative coordination to $H^+(CO)_{n-1}$ ($n \geq 4$) with the fixed structure of $H^+(CO)_2$. In fact, the fourth CO attacks the T-shaped $H^+(CO)_3$ to form $H^+(CO)_4$ with D_{2h} symmetry. The fifth and sixth CO's attack the plane of $H^+(CO)_4$ perpendicularly. In these clustering processes, the cation center of $H^+(CO)_2$ is attacked successively by σ lone-pair electrons of four CO's. In this respect, $H^+(CO)_2$ is a *shell* undeformed by the approach of CO's. Once $H^+(CO)_6$ is completed, further attack of CO is expected to be blocked by the coordinated CO's. This means that $H^+(CO)_7$ is much less stable than $H^+(CO)_6$, and indeed $H^+(N_2)_7$ was not detected experimentally even at very low temperature.[3] Another noticeable point of $H^+(CO)_n$ geometries is that the highest symmetry structures (D_{3h} for n = 3, D_{4h} or T_d for n = 4, D_{3h} for n = 5, and O_h for n = 6) are found to be extremely less stable than those in Figure 1a. This is because during $n - 1 \rightarrow n$, the geometrical deformation of $H^+(CO)_2$ brings about significant destabilization.

Concerning energetics of $H^+(CO)_n$ (Table IA), we have found some disagreement between $\Delta E_{n-1,n}$ and $\Delta H^\circ_{n-1,n}$. These discrepancies are explicable in terms of other factors given in the next section. For $H^+(N_2)_n$, surprisingly $\Delta E_{n-1,n}$ and $\Delta H^\circ_{n-1,n}$ are almost the same (Table IB). This coincidence is rather fortuitous, and the former is regarded as overestimated on the HF level. $\Delta E_{n-1,n}$ of both clusters reproduces the trend of $\Delta H^\circ_{n-1,n}$, i.e., it decreases very slowly with n (≥3). Usually, there is a gradual decrease of $\Delta H^\circ_{n-1,n}$ with charge dispersal through the addition of the neutral species.[5,6] For $H^+(CO)_n$ ($n \geq 3$), however, the cationic character of $H^+(CO)_2$ is maintained, and its attractive

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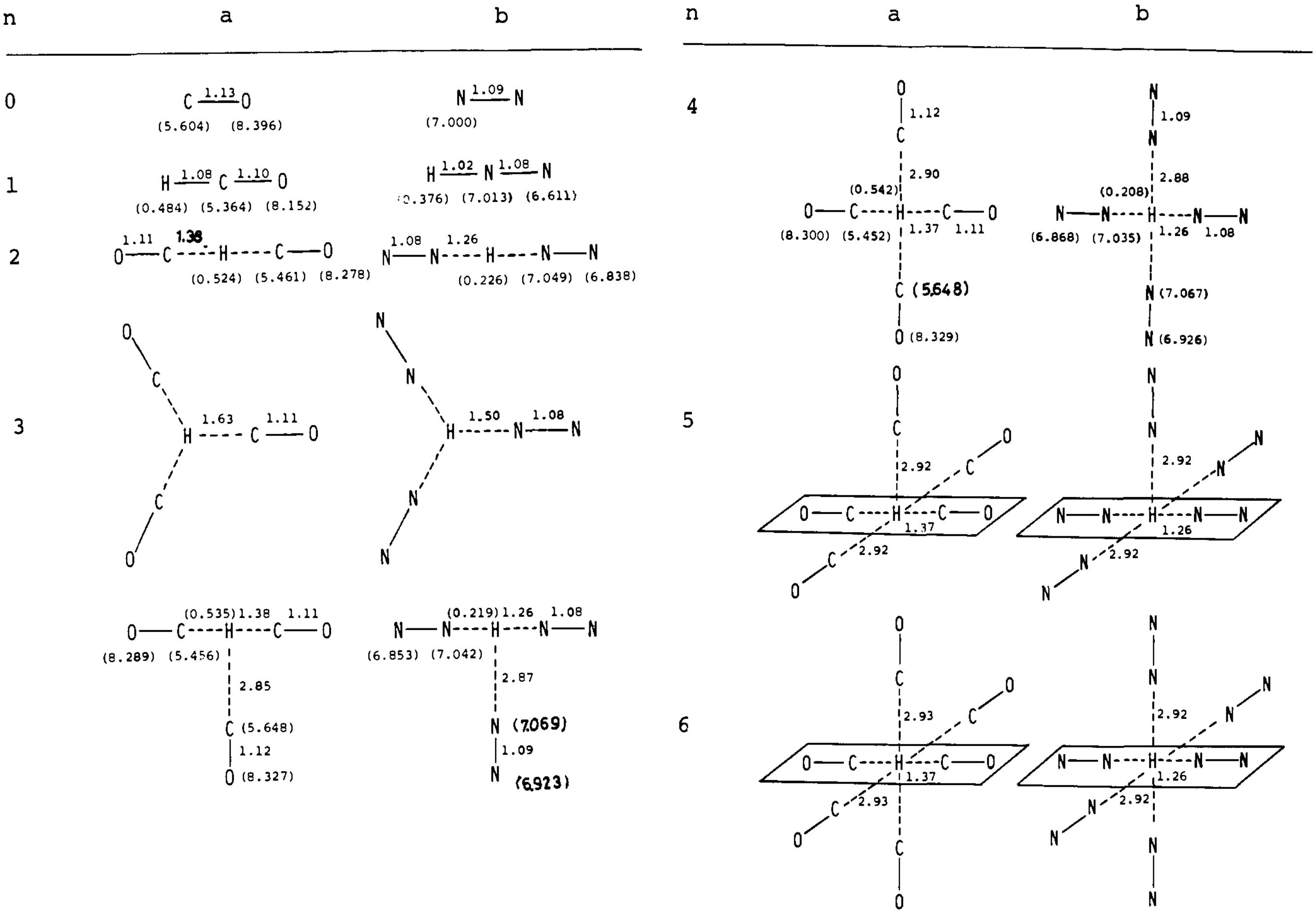

Figure 1. Geometries of $H^+(CO)_n$ and $H^+(N_2)_n$ optimized with the 4-31G RHF MO. Bond distances are in Å and numbers in parentheses are Mulliken atom populations. For $n = 5$ and 6, C–O and N–N bond lengths are fixed to those of $H^+(CO)_4$ and $H^+(N_2)_4$.

Table I. Total Energies (E_T's) and Stabilization Energies ($\Delta E_{n-1,n}$'s)

n	number of basis functions (4-31G)	cluster	point group of the cluster	E_T, au	$\Delta E_{n-1,n}$, kcal/mol	$\Delta H^\circ_{n-1,n}$, kcal/mol[a]
		A. $H^+(CO)_n$ Clusters for Optimized Geometries in Figure 1a				
0	18	CO	$C_{\infty h}$	−112.55237		
1	20	H^+CO	$C_{\infty h}$	−112.77933	−142.4	−139.0
2	38	$H^+(CO)_2$	$D_{\infty h}$	−225.34450	−8.0	−12.8
3	56	$H^+(CO)_3$	D_{3h}	−337.86688	18.8	
			C_{2v}	−337.90272	−3.7	−6.6
4	74	$H^+(CO)_4$	D_{2h}	−450.46094	−3.7	−6.3
5	92	$H^+(CO)_5$	C_{2v}	−563.01822	−3.1	−6.2
6	110	$H^+(CO)_6$	D_{2h}	−675.57486	−2.7	−5.8
		B. $H^+(N_2)_n$ Clusters for Optimized Geometries in Figure 1b				
0	18	N_2	$D_{\infty h}$	−108.75424		
1	20	H^+N_2	$C_{\infty h}$	−108.95026	−123.0	−113.7
2	38	$H^+(N_2)_2$	$D_{\infty h}$	−217.72957	−15.7	−16.0
3	56	$H^+(N_2)_3$	D_{3h}	−326.46086	14.4	
			C_{2v}	−326.48974	−3.7	−4.0
4	74	$H^+(N_2)_4$	D_{2h}	−435.24963	−3.6	−3.8
5	92	$H^+(N_2)_5$	C_{2v}	−544.00898	−3.2	−3.5
6	110	$H^+(N_2)_6$	D_{2h}	−652.76832	−3.2	−3.2

[a] Taken from ref 3.

power is not weakened by the addition of CO. This results in the nearly constant value of $\Delta H^\circ_{n-1,n}$ ($n = 3$–6). In particular, the Mulliken population of $H^+(N_2)_n$ ($n = 0$–4) exhibited in Figure 1b demonstrates clearly that $H^+(N_2)_2$ polarizes N_2's and its cationic character is rather increased so as to welcome more N_2's.

In Figure 3, the optimized structures of $H^+(O_2)_n$ ($n = 0$–4) are shown and Table II gives the energetics of the clusters. In Figure 3, H^+O_2 is bent because H^+ attacks favorably the sp^2 lone-pair electrons on the oxygen atom. For $H^+(O_2)_2$, two oxygen molecules share a proton in that direction. The difference of the spin multiplicities [i.e., $(2s + 1)$, s = spin quantum number] gives a negligible difference in the bond lengths, whereas the angle ∠HOO of $H^+(O_2)_2$ is somewhat affected. The third and the fourth O_2's attack the proton of $H^+(O_2)_2$ along the y axis very weakly, resulting in the polarization of the attacking species. For $H^+(O_2)_3$, the coordination of O_2 along the z axis is slightly less stable than that along the y axis. However, this energy difference is meaningless, because the C_{2h} $H^+(O_2)_2$ can rotate around the x axis almost freely, with $T > 0$ K. The feature of $H^+(O_2)_n$ clustering obtained by this MO calculation is that the third and the fourth O_2's are located linearly far from the proton of $H^+(O_2)_2$ to avoid the exchange repulsion and get the induction stability. In Table

Table II. E_T's and $\Delta E_{n-1,n}$'s of $H^+(O_2)_n$ Clusters for Optimized Geometries

n	cluster	spin quantum number, s, in $(2s + 1)$	point group of the cluster	E_T, au	$\Delta E_{n-1,n}$, kcal/mol	$\Delta H^\circ_{n-1,n}$, kcal/mol[a]
0	O_2	1	$D_{\infty h}$	−149.39299		
1	H^+O_2	1	C_s	−149.55692	−102.9	−101.0
		0		−149.49174		
2	$H^+(O_2)_2$	2	C_{2h}	−298.96906	−12.0	−20.0
		1		−298.79486		
		0		−298.82366		
3	$H^+(O_2)_3$	3	C_s	−448.36703	−3.1	−6.6
4	$H^+(O_2)_4$	4	C_{2h}	−597.76517	−3.2	−3.2

[a] Taken from ref 3.

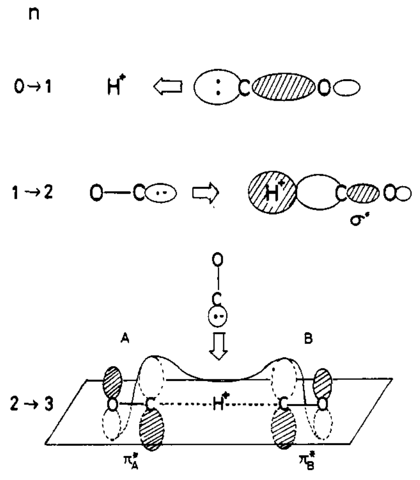

Figure 2.

II, the H^+O_2 and $H^+(O_2)_2$ results show that the state with the higher multiplicity gives the lower energy. For H^+O_2, E_T(triplet) is better than E_T(singlet), which indicates that the Hund's rule for the high-spin state is still effective, overcoming the orbital gap in the C_s symmetry. In view of E_T's of H^+O_2 and $H^+(O_2)_2$, the spin multiplicities of $H^+(O_2)_3$ and $H^+(O_2)_4$ are assumed to be 7 and 9, respectively. We cannot judge whether such high-spin states are realistic or not at the present time and must wait for a rigorous CI calculation. We calculated E_T for the $H^+(O_2)_5$ cluster where the fifth O_2 is along the z axis and the $H^+(O_2)_4$ structure (in the xy plane) is almost maintained. The cluster was reported to be not observed.[3] However, a small negative $\Delta E_{4,5}$ (~−2 kcal/mol) is obtained. In view of the fact that $\Delta E_{n-1,n}$ is smaller than $\Delta H^\circ_{n-1,n}$, it is supposed that $H^+(O_2)_5$ [and even $H^+(O_2)_6$] is present at $T = 0$ K. Of course, on the basis of this calculation alone, we cannot decide about the linkage of the weak $H^+(O_2)_4 \cdot \cdot O_2$ decisively. Qualitatively, it is natural that the stability of $H^+(O_2)_n$ decreases sharply as n becomes large, because O_2 (two more electrons than CO and N_2) provides the rich electron cloud, and

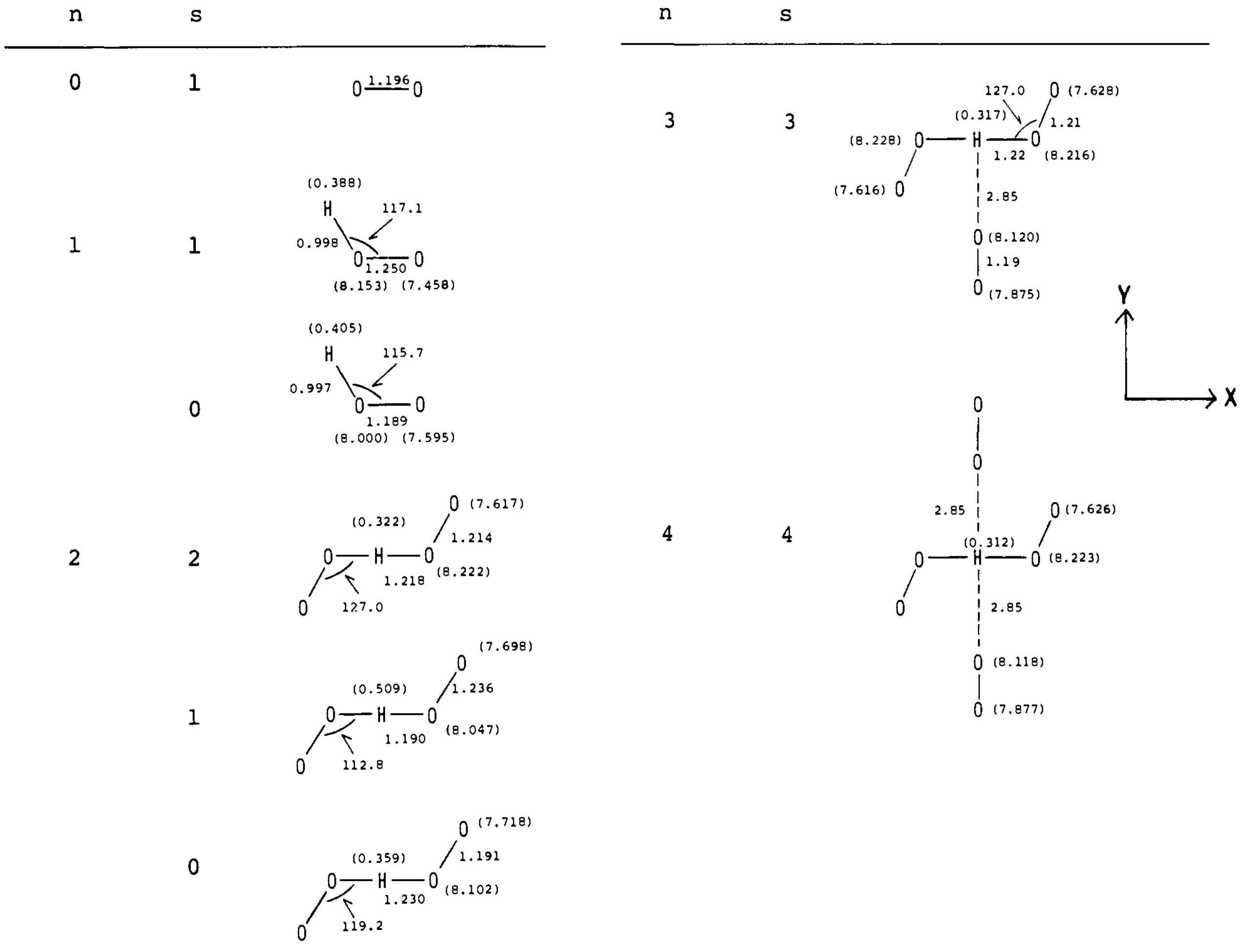

Figure 3. Geometries of $H^+(O_2)_n$ optimized with the 4-31G UHF MO. $\hat{S}^2\psi = s(s + 1)\psi$, where s is the spin quantum number.

Table III. Stabilization Energies ($\Delta E_{1,2}$'s) of $H^+(CO)_2$ and $H^+(N_2)_2$ Recalculated with the Correlation Effect[a]

clusters	point group	method	R, Å	E_T, au	$\Delta E_{1,2}$, kcal/mol	$\Delta H°_{1,2}$, kcal/mol
$O-C-H^+\cdots C-O$		HF	∞	−225.33170		−12.8
R	$D_{\infty h}$		1.38	−225.34450	−8.0	
	$C_{\infty h}$	CI	200.0	−225.71175		
	$D_{\infty h}$		1.39	−225.73115	−12.2	
$N-N-H^+\cdots N-N$		HF	∞	−217.70450		−16.0
R	$D_{\infty h}$		1.26	−217.72957	−15.7	
	$C_{\infty h}$	CI	200.0	−218.10292		
	$D_{\infty h}$		1.29	−218.13213	−18.3	

[a] The structures of H^+CO and H^+N_2 with CI are found to be almost the same as those with HF and are common to this calculation.

further attack of the O_2's is interfered with by this cloud around the proton.

Correlation Effect on $\Delta E_{1,2}$ of $H^+(CO)_2$ and $H^+(N_2)_2$

Some $\Delta E_{n-1,n}$'s on the HF level in Tables I and II are much smaller than $\Delta H°_{n-1,n}$'s. In particular, $\Delta E_{n-1,n}$'s (n = 3–6) of $H^+(CO)_n$ are only half the value of $\Delta H°_{n-1,n}$'s. For theoretical reproduction of $\Delta H°_{n-1,n}$, four terms should be taken into account.

$$\Delta H°_{n-1,n} = \Delta E_{n-1,n} + \text{correlation energy} + \text{difference of the zero-point vibrational energy} + \text{temperature correction}$$

To evaluate the energy of the electron correlation, we make a CI calculation for $H^+(CO)_2$ and $H^+(N_2)_2$. The CI result of the n = 2 systems is expected to give us a clue to the trend and degree of improvement for $\Delta E_{n-1,n}$. E_T's and $\Delta E_{1,2}$'s for $H^+(CO)_2$ and $H^+(N_2)_2$ obtained on the HF (already shown in Table I) and CI levels are summarized in Table III. In Table III, E_T's of H^+-$CO\cdots CO$ and $H^+N_2\cdots N_2$ at the larger intermolecular distance (R = 200 Å) are included. They are needed as reference points to determine $\Delta E_{1,2}$'s on the CI level. $\Delta E_{1,2}$ of $H^+(CO)_2$ on the HF level, −8.0 kcal/mol, is improved to −12.2 kcal/mol by the inclusion of the correlation correction. This turns out to be in good agreement with $\Delta H°_{1,2}$ (−12.8 kcal/mol). For $H^+(N_2)_2$, $\Delta E_{1,2}$ of −15.7 kcal/mol is corrected to −18.3 kcal/mol. The reoptimized intermolecular distances on the CI level are, however, almost the same as those on the HF level.

It is well-known that the estimation of the vibrational energy for the intermolecular new bond is extremely difficult. This is because for the shallow potential well the harmonic approximation becomes invalid. The contribution of the zero-point vibrational energy to the correction of the intermolecular bond energy is thought to be usually small (at most, a few kcal/mol).[7,8]. The temperature correction (T = 0–300 K) is of the order of RT and is expected to be within a few kcal/mol.

The CI result and such rough estimation indicate that the correlation correction is the most important factor to reproduce accurately $\Delta H°_{1,2}$. Thus, we may expect that the discrepancies between our HF $\Delta E_{n-1,n}$ and $\Delta H°_{n-1,n}$ ($n \geq 3$) are attributed mainly to the neglect of the electron correlation correction in these weakly bound systems.

For $H^+(CO)_2$ and $H^+(N_2)_2$, we have obtained the $D_{\infty h}$ geometries. If this assumption is removed, the position of the proton deviates slightly (~0.2 Å) from the center on the HF level. However, the CI calculation of $H^+(CO)_2$ gives a very shallow potential with respect to the movement of proton. It appears to require a more rigorous CI calculation (with the larger basis set) to check whether the linear structures of $H^+(CO)_2$ and $H^+(N_2)_2$ are symmetric ($D_{\infty h}$) or asymmetric ($C_{\infty h}$). A similar problem is found in H_5^+.[7] While the SCF result gives the C_{2v} structure, the CI gives the D_{2d} (symmetric) one.

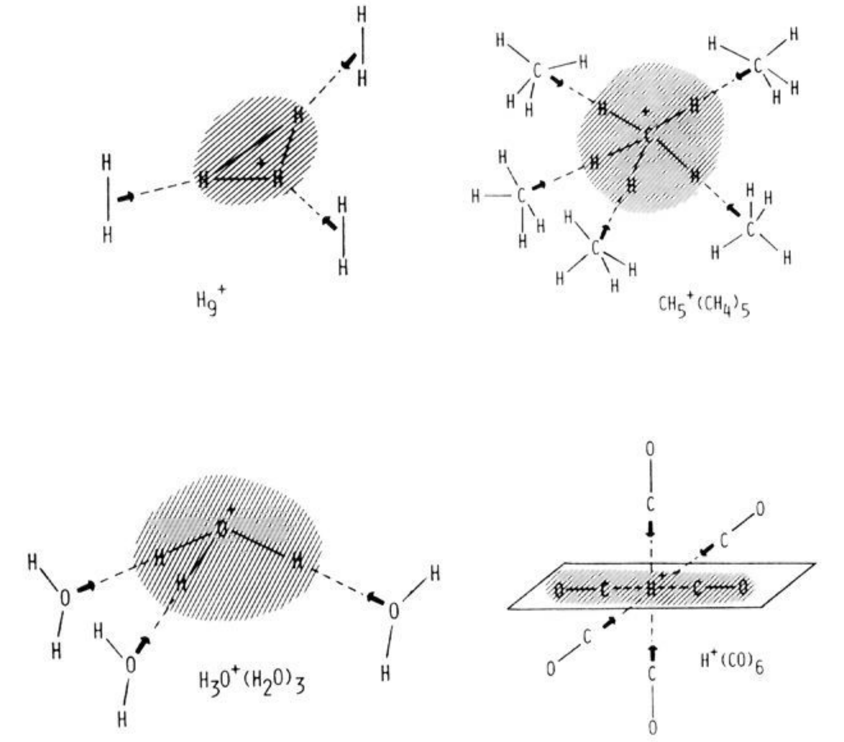

Figure 4. Schematic sketch of the mode of clusterings. The shaded part indicates the shell which is explained in the text.

Conclusion

On the basis of present results and other work done in this area [$H_3O^+(H_2O)_3$,[9] H_9^+ [10] and $CH_5^+(CH_4)_5$[11]], we may generalize the mechanism of the gas-phase clustering as follows:

(1) A proton is trapped into a neutral (parent) molecule, and the protonated species is prepared as a shell for clustering. For $H^+(CO)_n$, $H^+(N_2)_n$, and $H^+(O_2)_n$, the shell is completed when the σ bonds involving H^+ are formed.

(2) Once the shell is formed, the neutral molecules attack it weakly and successively (Figure 4). These bonds are caused mainly by induction stability (i.e., the polarization of the neutral molecules).

(3) The shell is surrounded by these molecules in such a way that the cationic nature is blocked from all directions. At this stage, further clustering is prohibited or even if it exists, the new bond should be very weak. Through a perturbation of the temperature effect ($T \gg 0$ K), this bond would be easily broken and not observed. When the parent molecule is polar (e.g., H_2O), clustering is not constrained to the shell and the surroundings on account of the Coulombic attraction.

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