Structure and Nature of the Interaction of the $CH_3N_2^+$ Ion Shellvated by H_2 Molecules: $CH_3N_2^+(H_2)_{n=1-9}$

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The existence of $CH_3N_2^+(H_2)_n$ complexes is predicted for n up to 9. The structures, dissociation energies, and vibrational frequencies of these complexes are studied, particularly focusing on the shellvation phenomenon. The formation of clusters is based on the consecutive filling of three distinct shells. Because of very similar stabilization energies in all shells, all possible occupations are studied. Hydrogen molecules belonging to the same shell possess similar properties, which is shown on the basis of dissociation energies, vibrational frequencies, and a study of the interaction energy decomposition.

1. Introduction

Studies of the properties of ionic clusters formed in the gas phase by the consecutive attachment of uncharged species to the central anion elucidate the properties of these species and their relationship to condensed-phase analogues.[1] In the case of $(NH_2)^-(NH_3)_n$ interactions, only two molecules of NH_3 are needed to reverse the order of basicity from that of bare anions to that found in solution.[2,3] However, the thermodynamics of solvation processes is based on the balance between the ion−molecule interactions and intermolecular interactions. In the case of solutions the intermolecular interactions are sufficient to produce liquid without the addition of solute species. On the other hand, some molecules, candidates for coordination by ions in the gas phase, interact weakly and do not become liquid under mild conditions. The molecular hydrogen interacting with CH_3^+ is an example of such a moiety. It has been shown[4] that the carbonium cations $CH_3^+(H_2)_n$ exist for n as large as 6. In such complexes the interactions between coordinated molecules are negligible, and the existence of the cluster structure is totally determined by the ion-generated field. The nature and symmetry of the ion-generated field leads to the specific shell structure of the ion−(molecule)$_n$ clusters. The term solvation, which is suitable for ionic clusters leading to the liquid solution (the media for which the name was created), seems to be inadequate for the case when ion coordinates noninteracting molecules. As can be concluded from the presented data, in the gas phase the process of forming shells is almost entirely determined by the core ion. The name "shellvation" was proposed[12] for the latter case. Most of the experimental studies performed until now were focused on the production of cations coated with one type of molecule.[5] Since the structure of the cluster is determined by the electric field of the central cation, the modification of such a field could lead to entirely different structures. The aim of this work is an exploration of the possible role of modifications of the central ion field in the formation of clusters. The existing studies for $H^+(H_2)_n$ and $H^+N_2(H_2)_n$ clusters indicate an interesting change in the cluster properties when the field of H^+ is modified by the nitrogen molecule.[6−8] In our studies we have selected the CH_3^+ cation, since it produces a significantly more complex electric field compared to H^+, modified by the N_2 molecule. The parent cluster $CH_3^+(H_2)_n$ was extensively studied experimentally and theoretically[1,9−11] and may be used as a reference moiety. The results of the aforementioned theoretical studies are in very good agreement with the experimental data and allow for the assumption that a similar approach will prove to be successful also in this work. The reaction of CH_3^+ with N_2 leads to a stable analogue of CH_3CN. The similar cation $CF_3N_2^+$ is known to produce[13] clusters by the coordination of N_2.

In this paper we study the structure, vibrational properties, dissociation energies, and nature of interaction of the $CH_3N_2^+$ cation shellvated by hydrogen molecules. We discuss the properties of the $CH_3N_2^+(H_2)_{n=1-9}$ system, focusing our attention on the shellvation phenomenon. This study could be a guide for future experimental investigations of $CH_3N_2^+(H_2)_{n=1-9}$ complexes.

2. Details of the Theoretical Treatment

All calculations carried out in this paper were performed using a standard 6-311(d,p) basis set.[14−16] The geometries of the studied complexes were optimized at the second-order Moller−Plesset[17] perturbation level of theory using analytical gradients. The harmonic vibrational frequencies were also obtained at the MP2 level of theory from analytical second-order derivatives. The dissociation energies were calculated within the second-order Moller−Plesset perturbation theory (MP2), and the results were corrected for the nonphysical basis set superposition error (BSSE) by means of the counterpoise correction scheme proposed by Boys and Bernardi.[18]

The frequencies and thermodynamical functions were calculated by applying the ideal gas, rigid rotor, and harmonic oscillator approximation[19] for normal conditions. The nature of interactions was studied using the variation−perturbation energy decomposition scheme proposed by Sokalski et al.[20] In this approach the SCF interaction energy is partitioned into the first-order electrostatic $E_{EL}^{(1)}$, first-order exchange $E_{EX}^{(1)}$, and the higher order deformation $E_{DEF}^{(R)}$ energy terms consistently

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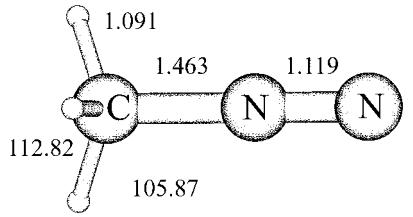

Figure 1. Structure of the core cation$-CH_3N_2^+$. Distances are in angstroms, and angles are in degrees.

defined in the dimer basis set. The $E_{DEF}^{(R)}$ term accounts for the charge transfer and polarization interactions.[20] To take into account the correlation energy, the former scheme was augmented with E_{CORR}, which includes all intermolecular (dispersion) and higher order correlation energy components and is defined as the difference between the MP2 and SCF interaction energies. The interaction energy decomposition scheme was implemented in the GAMESS program.[21] All other results presented in this work were obtained by utilizing the Gaussian 94 code.[22]

3. Results and Discussion

3.1. Structure of Shells. It has been shown[10,11] that the optimized geometries of complexes similar to those studied in this work obtained at the MP2/6-311G(d,p) level are reliable, and only slight changes are expected by enhancement of the level of theory or by utilizing a more flexible basis set. There were no constraints imposed during the geometry optimizations due to the molecular symmetry. The location of the true minima was ensured by the computation of the Hessian matrix.

The ground state for the $CH_3N_2^+$ cation was found to be a covalently bound system of C_{3v} symmetry (Figure 1) contrary to that of the $CH_3^+(H_2)$ and $SiH_3^+(H_2)$ species, which are weakly bound complexes.[10,23] The nitrogen molecule is bound to the carbon atom of the CH_3^+ core, forming a strong covalent bond characterized by a length of 1.46 Å and a dissociation energy

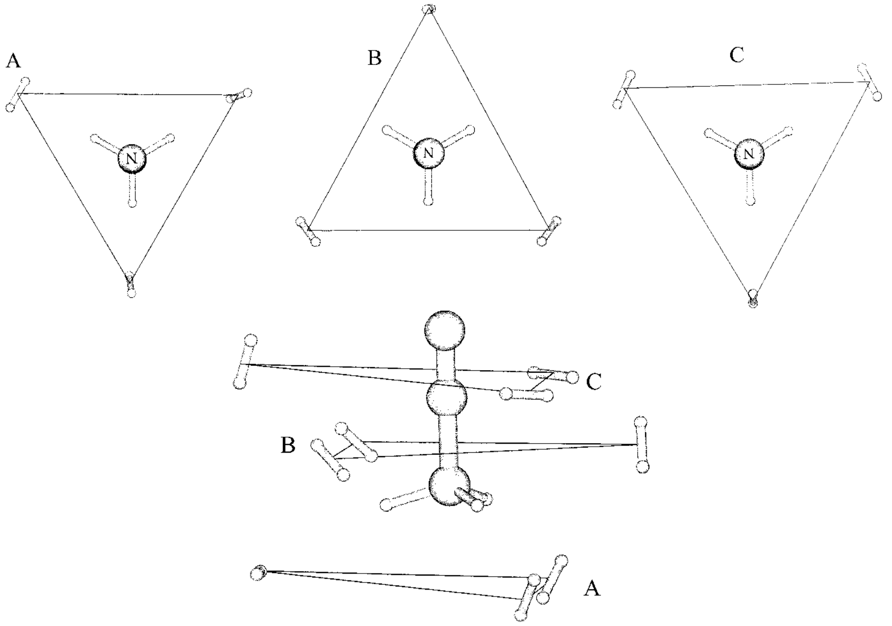

Figure 2. Overall structure of shells for the $CH_3N_2^+(H_2)_9$ complex.

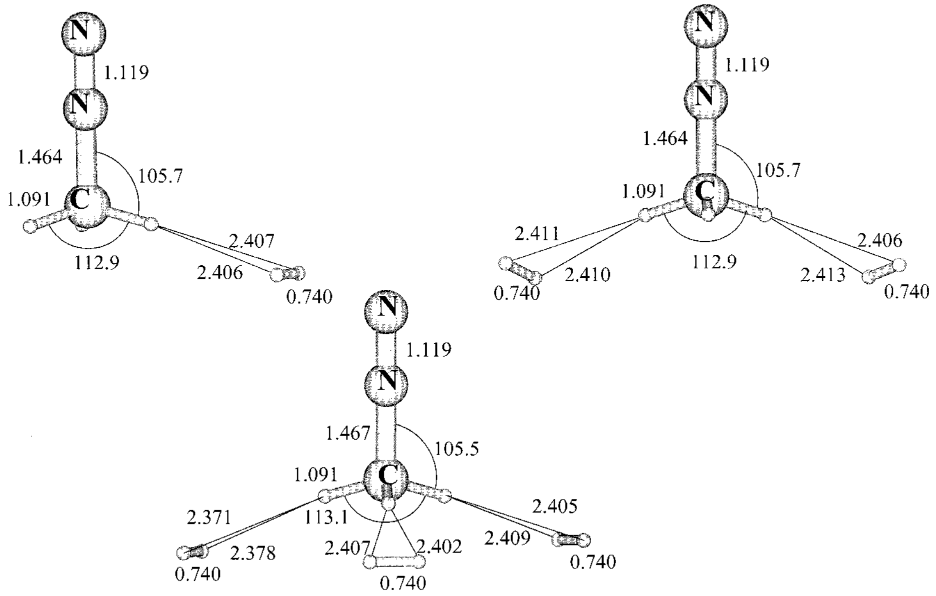

Figure 3. Structures of consecutively occupied shell A. Distances are in angstroms, and angles are in degrees.

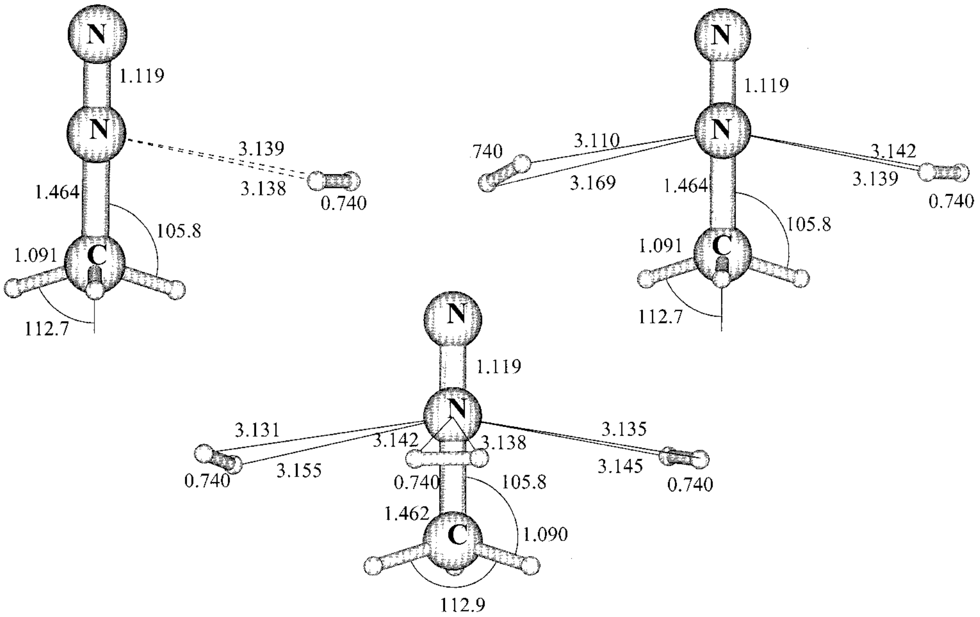

Figure 4. Structures of consecutively occupied shell B. Distances in are angstroms, and angles are in degrees.

TABLE 1: Consecutive and Total MP2 Dissociation Energies (D_e) for the Occupation of Single Shells[a]

occupation			D_e		D_e^b	
A	B	C	consecutive	total	consecutive	total
			Shell A			
1	0	0	0.037	0.037	0.031	0.031
2	0	0	0.036	0.073	0.030	0.061
3	0	0	0.036	0.109	0.030	0.091
			Shell B			
0	1	0	0.034	0.034	0.029	0.029
0	2	0	0.034	0.069	0.029	0.058
0	3	0	0.034	0.103	0.029	0.088
			Shell C			
0	0	1	0.034	0.034	0.030	0.030
0	0	2	0.034	0.067	0.029	0.059
0	0	3	0.033	0.100	0.029	0.088

[a] All values are in eV. The occupations of particular shells are given in the first three columns. [b] Corrected for the BSSE, all electrons correlated.

TABLE 2: Consecutive and Total MP2 Dissociation Energies (D_e) for Mixed Occupation of Shells[a]

shell occupation			D_e		D_e^b	
A	B	C	consecutive	total	consecutive	total
			Shells A and B			
1	3	0	0.037	0.141	0.031	0.118
2	3	0	0.037	0.178	0.030	0.148
3	3	0	0.037	0.215	0.030	0.177
3	**1**	0	0.035	0.144	0.029	0.120
3	**2**	0	0.035	0.179	0.029	0.148
3	**3**	0	0.035	0.215	0.028	0.177
			Shells B and C			
0	1	**1**	0.034	0.068	0.029	0.058
0	1	**2**	0.033	0.101	0.029	0.087
0	2	2		0.136		0.115
0	3	**1**	0.032	0.135	0.029	0.115
0	3	**2**	0.030	0.166	0.028	0.141
			Shells A, B, and C			
1	1	2		0.138		0.117
1	2	2		0.173		0.145
1	3	1		0.173		0.145
2	2	1		0.176		0.147
2	3	1		0.210		0.174
3	3	**1**	0.028	0.243	0.025	0.199
3	3	**2**	0.025	0.268	0.021	0.218
3	3	**3**	0.024	0.291	0.020	0.238

[a] All values are in eV. The occupations of particular shells are given in the first three columns. Consecutive values correspond to the boldfaced occupation numbers. [b] Corrected for the BSSE, all electrons correlated.

of 67.5 kcal/mol. The structure of such a core cation is virtually unperturbed by the attachment of consecutive hydrogen molecules.

We have obtained the equilibrium structures of the $CH_3N_2^+$-$(H_2)_n$ complexes up to $n = 9$. Three possible shells A, B, and C (Figure 2) were determined with each of them capable of hosting up to three H_2 molecules. Although the binding energies differ between shells, the difference is small enough that there can be no definite answer on the question of what will be the preferred structure of a complex for a given number of shellvent molecules. Therefore, we have studied all possible occupations of shell pairs (AB, AC, and BC).

The first shell, A (Figure 3), is energetically the most stable and consists of up to three hydrogen molecules forming T bonds between their center of mass (c-o-m) and the hydrogens of the core cation. The second shell, B, may host up to three hydrogen molecules captured in equivalent energetic cages that lie on a plane perpendicular to the CNN axis (Figure 4). The distance between the c-o-m of the H_2 molecules and the nitrogen atom is almost the same for all three cages. Hydrogen molecules are likely to rotate almost freely around the nitrogen−H_2 c-o-m axes. The energy variations between isomers characterized by different occupations of the A and B shells are small (Table 2), and a variety of clusters of different occupation are energetically equivalent. In fact the most stable isomer is often due to small but favorable interactions between molecules already occupying the shells. The structure of the last shell, C (Figure 5), is similar to B, but the plain is slightly higher now and the positions of hydrogen molecules are rotated by approximately 60° compared to those of shell B. The stabilization energies listed in Table 1 suggest that the hydrogen molecules trapped in shell C should have similar properties to those in shell B. However, the occupation of other shells influences strongly the interactions in shell C. Although we have found few structures in which shell C was occupied together with partially filled shells A and

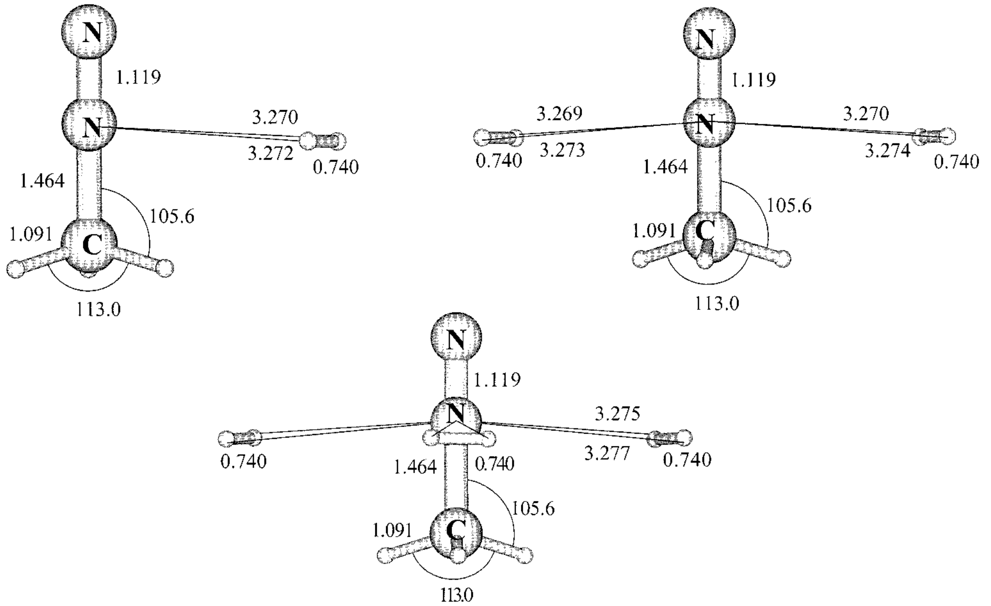

Figure 5. Structures of consecutively occupied shell C. Distances in are angstroms, and angles are in degrees.

TABLE 3: H−H Harmonic Vibrational Frequencies of H_2 Molecules within Shells[a]

occupation no.			vibrational frequencies								
A	B	C	shell A			shell B			shell C		
			Free Hydrogen								
	4534										
			One Shell Occupied								
1	0	0	4503								
2	0	0	4504	4504							
3	0	0	4504	4504	4504						
0	1	0				4515					
0	2	0				4515	4515				
0	3	0				4515	4515	4515			
0	0	1							4512		
0	0	2							4512	4512	
0	0	3							4512	4512	4512
			Two Shells Occupied								
1	3	0	4505			4515	4515	4515			
2	3	0	4505	4505		4515	4515	4515			
3	1	0	4504	4505	4505	4516					
3	2	0	4504	4505	4506	4514	4515				
3	3	0	4505	4505	4506	4516	4516	4516			
0	3	1				4515	4515	4515	4514		
0	3	2				4515	4515	4516	4514	4514	
			Three Shells Occupied								
1	1	2	4504			4516			4512	4513	
1	2	2	4507			4513	4514		4515	4515	
1	3	1	4505			4515	4515	4516	4514		
2	2	1	4505	4505		4516	4516		4513		
2	3	1	4506	4506		4515	4516	4516	4516		
3	3	1	4506	4507	4510	4515	4515	4516	4518		
3	3	2	4506	4507	4510	4515	4517	4517	4518	4521	
3	3	3	4506	4510	4510	4517	4517	4517	4519	4519	4521

[a] The occupations of particular shells are given in the first three columns. Units for frequencies are in cm^{-1}.

TABLE 4: Decomposition of the Interaction Energies in the $CH_3N_2^+(H_2)_{n=1-3}$ Complexes[a]

interaction energy components	1	2		3	
	total	consecutive	total	consecutive	total
Shell A					
ΔE_{HL}	0.011	0.011	0.022	0.011	0.031
$E_{EL}^{(1)}$	−0.030	−0.029	−0.059	−0.029	−0.088
$E_{EX}^{(1)}$	0.041	0.041	0.081	0.040	0.119
$E_{DEF}^{(R)}$	−0.028	−0.028	−0.056	−0.027	−0.082
ΔE_{SCF}	−0.017	−0.016	−0.034	−0.016	−0.051
E_{CORR}	−0.014	−0.014	−0.027	−0.014	−0.041
ΔE_{TOT}	−0.031	−0.030	−0.061	−0.030	−0.091
Shell B					
ΔE_{HL}	0.008	0.008	0.016	0.008	0.023
$E_{EL}^{(1)}$	−0.030	−0.030	−0.060	−0.030	−0.089
$E_{EX}^{(1)}$	0.038	0.037	0.075	0.038	0.113
$E_{DEF}^{(R)}$	−0.018	−0.018	−0.036	−0.018	−0.054
ΔE_{SCF}	−0.010	−0.010	−0.020	−0.010	−0.030
E_{CORR}	−0.019	−0.019	−0.038	−0.019	−0.057
ΔE_{TOT}	−0.029	−0.029	−0.058	−0.029	−0.088
Shell C					
ΔE_{HL}	0.000	0.000	0.000	0.000	−0.001
$E_{EL}^{(1)}$	−0.029	−0.029	−0.058	−0.029	−0.087
$E_{EX}^{(1)}$	0.029	0.029	0.058	0.029	0.086
$E_{DEF}^{(R)}$	−0.016	−0.016	−0.031	−0.016	−0.046
ΔE_{SCF}	−0.016	−0.016	−0.032	−0.015	−0.047
E_{CORR}	−0.014	−0.014	−0.028	−0.014	−0.041
ΔE_{TOT}	−0.030	−0.029	−0.059	−0.029	−0.088

[a] Only one shell at a time is occupied. The numbers in the first row are the occupation numbers. All values are in eV. Negative values correspond to attractive interactions.

B (Figure 6), this shell probably will be occupied only when shells A and B will be already fully occupied or in the case of very small clusters ($n = 1-3$). In particular, when shell A was even partially occupied, we were unable to find structures in which the corresponding positions in shell C (i.e., above hydrogen molecules trapped in shell A) were also occupied. During the geometry optimization of complexes in which shells A and B were not entirely filled up, hydrogen molecules from shell C usually took up positions in shells A or B unless all neighboring positions in those shells were occupied or the size of the cluster was relatively small. In the case of large clusters in which shells A and B are fully occupied (Figure 6, clusters 331, 332, and 333), the presence of hydrogen molecules in shell A destabilizes the adjacent hydrogens in shell C, which is indicated by the lowering of total dissociation energies and the overall changes in the H−H stretching vibrations within shell C (Tables 2, 3, 5) relative to smaller clusters.

Generally, the H_2 molecules in the cluster possess significant rotational freedom and are likely to scramble through very low-lying transition states. Although the position of the shellvent molecule is not definite, the structure and energetics of the shell systems are quite well defined, and the bonding process can be

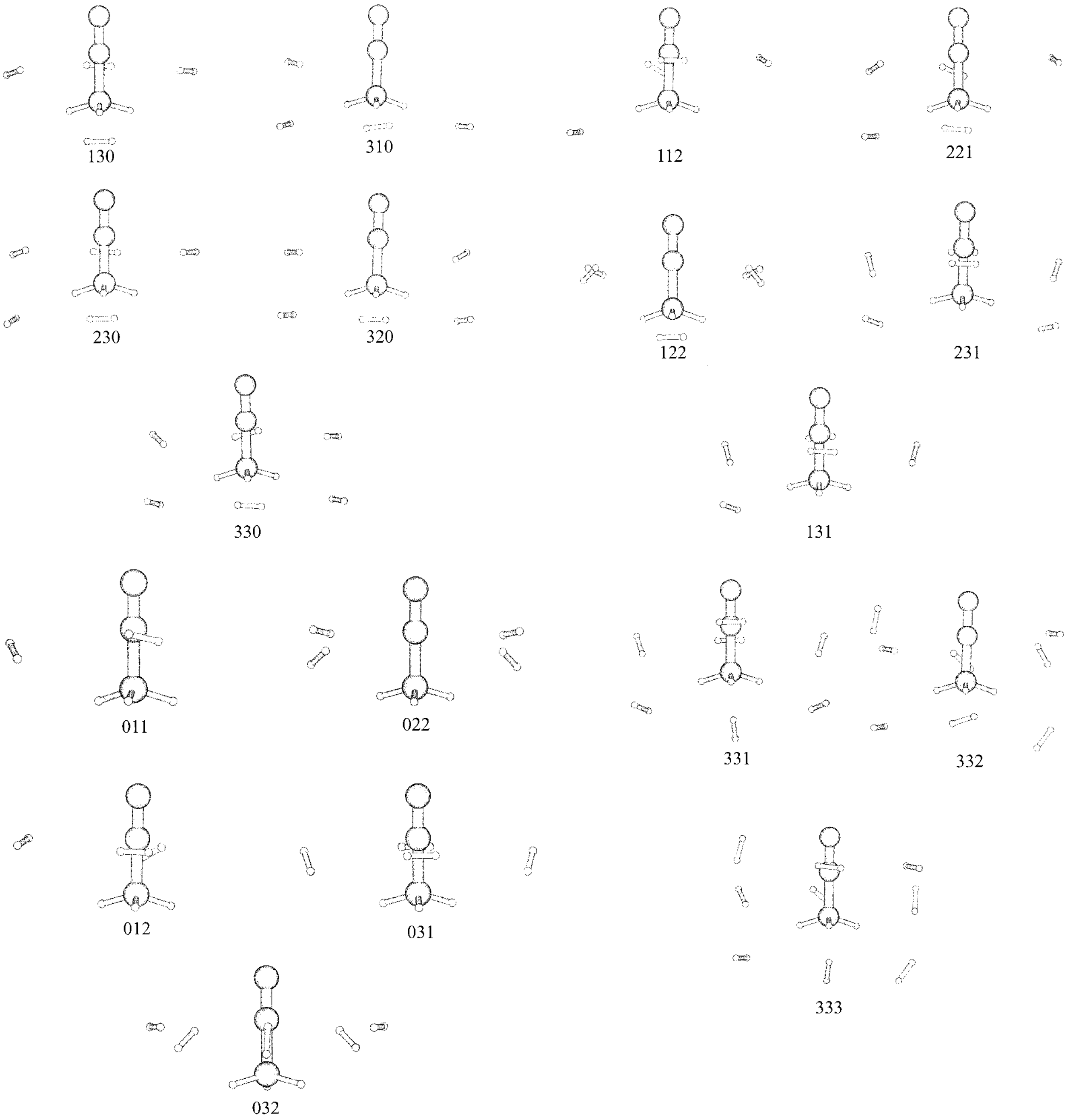

Figure 6. Schematic structures of the complexes listed in Table 2. The labels refer to the occupations of shells A, B, and C, respectively.

regarded as trapping the molecule in an energetic cage. In additon, the H_2 molecules trapped in the complex sustain their nature rather well, and the H−H bond distance increases only slightly from 0.70 Å in a free molecule to 0.74 Å in a complex.

3.2. Energetics. The values of the dissociation energies presented in this work should be considered qualitatively. The quantitative calculations of dissociation energies require advanced theoretical techniques and extensive basis sets and hence are restricted to small systems. The available theoretical results for similar systems indicate[11,12] that the enhancement of the applied level of theory results generally in an increase in the computed values of dissociation energies. The dissociation energy of a single H_2 molecule from A, B, and C shells is about 0.03 eV and is sufficiently large to detect the shellvents experimentally. The dissociation energies are similar for molecules occupying different shells (Tables 1 and 2) and, because of the possible mixed occupations of the shells, result in a large number of isomers.

The vibrational frequencies are very sensitive to the nature of bonding and the environment of the shellvated molecule in the structural skeleton. Although the values of frequencies may be treated only qualitatively because of its sensitivity to the level of theory applied and the proper accounting for anharmonicity,[4] they indicate the presence of the A shell as being distinct from the others (Table 3). The values of the H−H stretching vibrations are identical within the shells and do not depend on the occupation of those shells. The difference between shells is well preserved when the mixed shells are occupied.

The structures and vibrational properties discussed previously confirm our assumption of the shell nature of the $CH_3N_2^+$-$(H_2)_{n=1-9}$ clusters. Such a model is also confirmed by the calculated bonding properties (Tables 4 and 5). The core $CH_3N_2^+$ cation binds hydrogen molecules mainly because of electron correlation effects, and the SCF interaction energy is usually an order of magnitude smaller. Electrostatic interaction, although negative (i.e., attractive), is in all cases smaller than

TABLE 5: Decomposition of the Interaction Energies in the $CH_3N_2^+(H_2)_9$ Complex When All Shells Are Fully Occupied (i.e., between Each H_2 Molecule Consecutively and the Rest of the Complex)[a]

interaction energy component	shell A			shell B			shell C		
	1	2	3	1	2	3	1	2	3
ΔE_{HL}	0.014	0.013	0.013	0.014	0.014	0.014	0.009	0.009	0.009
$E_{EL}^{(1)}$	−0.031	−0.027	−0.027	−0.030	−0.030	−0.025	−0.032	−0.031	−0.020
$E_{X}^{(1)}$	0.045	0.040	0.040	0.044	0.044	0.039	0.041	0.040	0.029
$E_{DEF}^{(R)}$	−0.025	−0.022	−0.022	−0.016	−0.016	−0.016	−0.013	−0.013	−0.010
ΔE_{SCF}	−0.011	−0.009	−0.009	−0.002	−0.002	−0.002	−0.004	−0.004	−0.001
E_{CORR}	−0.018	−0.017	−0.017	−0.024	−0.024	−0.023	−0.020	−0.020	−0.019
ΔE_{TOT}	−0.029	−0.026	−0.026	−0.026	−0.026	−0.025	−0.024	−0.024	−0.020

[a] All values in eV. Negative values correspond to attractive interactions.

the exchange repulsion term. The total Heitler−London interaction energy cancels out to a large extent the deformation part of the SCF interaction energy. The deformation term ($E_{DEF}^{(R)}$) arising from the SCF decomposition is the most sensitive property concerning shell occupation (Tables 4 and 5). The correlation part of interactions (from the MP2 calculations) indicates the dominant role of dispersion forces. These interactions are found to be shell-specific.

4. Conclusions

The former studies indicate[5−9] that the structures of cationic clusters of noninteracting shellvent molecules are almost entirely determined by the properties of the electric field of the central ion. A modification of this field would lead to significantly modified structures and would permit the modeling of new clusters. The interactions of CH_3^+ with H_2 were extensively studied. The clusters based on the CH_3^+ cation, with an electric field modified by the attachment of the N_2 molecule and H_2 molecules, were studied in this paper. The $CH_3^+ + N_2$ reaction leads to the $CH_3N_2^+$ cation, an analogue of the CH_3CN molecule. The shell structure found for such a moiety is totally different from those formed by the parent CH_3^+ cation.[10,11]

The interaction of the $CH_3N_2^+$ cation with the H_2 molecules leads to complexes with well-defined shell structures. In the case of the studied $CH_3N_2^+(H_2)_{n=1-9}$ system, three distinct shells have been recognized with a shell occupation of a maximum of three hydrogen molecules. The molecules trapped within the same shell possess similar dissociation energies and vibrational frequencies. The nature of interactions observed within the shells is virtually the same. The properties of the molecules occupying the same shell are almost entirely determined by the field of the central ion, and only slight perturbations were observed coming from the neighboring molecules. The molecules forming the shell system often possess significant rotational freedom, and the structure of shellvated systems is not definite. The molecules trapped in shell cages are likely to rotate through a number of low-lying transition states.

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