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Ab initio calculation of the electronic spectrum and ionization potentials of hydrazine

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Abstract

Ab initio calculations for electronic states of hydrazine are reported. The VUV spectrum is analyzed. The first transitions are all Rydberg transitions and the first valence states are only expected above 10 eV. The first five vertical ionization potentials are reported. The structural properties of the $N_2H_4^+$ ion conformers are discussed. © 1997 Elsevier Science B.V.

1. Introduction

In a previous publication, Syage et al. [1] have reported results aimed at a detailed interpretation of electronic spectra of hydrazines including the determination of their threshold of photoionization potentials. These experimental results are in good agreement with those already known [2,3]. There are several ab initio calculations on ground state N_2H_4 [4–10]. Unfortunately, theoretical results concerning the excited electronic states do not allow a complete interpretation of spectroscopic data. The only available ab initio calculations are those obtained by Staemmler [11] who studied the C_2 symmetry, experimentally and theoretically known as the most stable structure, some Rydberg excitations involving particularly the 3s level. The hydrazine VUV absorption spectrum presents three broad bands without any vibrational structure at 195, 170 and 130 nm. Compared to the first results obtained by Schürgers and Welge [2], the spectrum published by Syage et al. shows three more poorly defined shoulders at 218 and 178 nm and 155 nm. A similar spectrum was obtained by Hopkirk et al. [12] for the isotopic compound N_2D_4 using synchrotron radiation. The assignment of the electronic spectrum of N_2H_4 proposed by Robin [13] underlines the Rydberg nature of the lowest lying electronic states. The transition at 190 nm is proposed as the first term in the Rydberg series converging towards the lowest vertical ionization potential involving the symmetric combination n_+ of nitrogen lone pairs ($3s_R \leftarrow n_+$), while the band observed at 170 nm is assigned to Rydberg series ($3s_R \leftarrow n_-$) converging towards the second vertical ionization potential. The assignment by Syage et al. of the hydrazine electronic spectrum is based on the assumption that N_2H_4 excitations roughly follow D_{2h} selection rules (corresponding to a geometrical relaxation leading to planar excited states). Although the analysis of this previous work is quite satisfactory, many theoretical aspects remain to be defined, such as the nature of the electronic states, the evaluation of the oscillator strengths, or

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the possible overlapping of Rydberg and valence transitions.

The aim of the present work is to provide theoretical data that could rationalise and complement all the experimental results already obtained. This report includes a study of the hydrazine electronic spectrum in C_2 and D_{2h} structures and the calculation of its ionization potentials.

2. Computational method

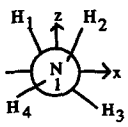
The molecular wave functions calculations result from an ab initio treatment. All the theoretical calculations on electronic excited states have been performed with the CIPSI algorithm [14] which combines variational and perturbational processes for a MRSDCI multireference wave function. The part of the correlation energy resulting from the quadriexcitations of the reference subspace and not taken into account at the MP2 level has been evaluated from the formalism first proposed by Davidson [15] and extended by Buenker and Peyerimhoff [16]. The corresponding results refer to the MRSDQCI label. Moreover for the ionization potentials, a series of calculations with a multiconfigurational second order perturbation theory (CASPT2) have been performed with the MOLCAS program [17]. Most of these results have been obtained with a 6-31G* [18] Gaussian basis set extended by addition of diffuse functions centered on the middle of the N–N bond, the exponents ($\alpha_s = 0.022$; $\alpha_p = 0.021$; $\alpha_d = 0.013$; $\alpha'_s = 0.0055$) of which were optimized. In order to compare the influence of the basis set, many results obtained from the Gaussian basis sets proposed by Huzinaga and contracted according to Dunning et al. [19] will be discussed.

3. Results and discussion

3.1. Ionization potentials

In the hydrazine photoelectron spectrum two large bands without vibrational structure are observed, each of them corresponding to two well resolved peaks: at least they correspond to four bands resulting from the first four vertical IPs respectively measured at 9.91, 10.64, 15.61 and 16.56 eV. Many theoretical calculations have been performed [4–10]. The calculated splitting between the first two ionization potentials is always lower than the experimental values [20,21] (0.2–0.5 eV against 0.4–0.7 eV). The best known calculation has been published by Staemmler (9.57 eV and 10.03 eV) at the Hartree–Fock (HF) level. To provide theoretical data that could account for electronic spectra we must first precisely evaluate the vertical IPs. We report in Table 1 our results concerning the structural geometry of N_2H_4. For hydrazine, the structural parameters have been fully optimized at different levels of calculation (MP2, MCSCF, CASPT2) with different basis sets 6-31G*,

Table 1
Basis set influence on the optimized structural parameters of hydrazine for (C_2) pyramidal gauche geometry with respect to the non-bonding orbitals. Bond lengths are in Å and angles in degrees

		MP2		MCSCF	CASPT2		
		6.31G*	TZP	TZP	TZP	Exp.	
E (au)		−111.50416	−111.62579	−111.35489	−111.66003	[22]	[23,24]
	N_1N_2	1.439	1.443	1.471	1.449	1.453	1.449
	N_1H_2	1.021	1.018	1.023	1.016	1.02	1.022
	N_1H_4	1.017	1.014	1.019	1.018	1.02	1.019
	$H_2N_1N_2$	111.42	111.00	109.50	110.74	112.0	112 ± 2
	$H_4N_1N_2$	106.29	106.25	105.18	106.03	–	106 ± 2
	H_2NH_4	106.90	106.69	105.76	106.62	105.8	106.6
	H_2NNH_3 (θ)	90.53	90.55	90.65	90.44	90–95	91 ± 2
	H_1NNH_2	25.57	25.06 (26.07) [a]	22.60	24.85	–	

[a] Addition of f and p polarization functions ($\alpha_f = 1.093$, $\alpha_p = 1$) respectively on N and H.

Table 2
Vertical ionization potentials of N_2H_4 (eV) as a function of approximation level and basis set. Comparison with vertical experimental ones. The N_2H_4 electronic ground state configuration $\tilde{X}$ (^1A) at the HF level for C_2 is given by: $1a^2\ 1b^2 2a^2 2b^2\ 3a^2\ 3b^2\ 4a^2 4b^2\ 5a^2$

Ionic state[2]	Configuration [a]	ΔE [b]	ΔE [c]	ΔE [d]	ΔE [e]	exp. [f]
A	... $3a^2\ 3b^2\ 4a^2\ 4b^2\ 5a$	11.0	10.03	10.15	9.77	9.91
^2B	... $3a^2\ 3b^2\ 4a^2\ 4b\ 5a^2$	11.4	10.30	10.32	9.99	10.64
^2A	... $3a^2\ 3b^2\ 4a\ 4b^2\ 5a^2$	–	–	–	15.48	15.61
^2B	... $3a^2\ 3b\ 4a^2\ 4b^2\ 5a^2$	–	–	–	16.86	16.66
^2A	... $3a\ 3b^2\ 4a^2\ 4b^2\ 5a^2$	–	–	–	17.14	

[a] Most important configuration in the multiconfigurational wave function.
Calculated energies relative to the ground state of N_2H_4:
[b] Koopman's theorem: mean values (± 0.2 eV) obtained with different basis sets (6-31G*, 6-31G**, TZP). The splitting between the first two IPs is from 0.2 to 0.25 eV.
[c] CASPT2 level with N: 10s 6p 2d | 5s 3p 2d; H: 5s 1p | 3s 1p. Ref. [19].
[d] CASPT2 level with N: 10s 6p 2d 1f | 5s 3p 2d 1f; H: 5s 1p | 3s 1p. Ref. [19].
[e] MRSDQCI level and 6-31G* basis set.
[f] Refs. [20,21].

TZP [18,19] but without Rydberg type orbitals, only used for the interpretation of the electronic spectrum. Our results are in the range of several other calculations and experimental results. We can observe that the structural parameters are slightly affected by the choice of the orbital basis set. In particular, the dihedral angle θ which governs the lone pairs interaction is quite constant ($90° \pm 1$). Even the addition of f and p polarization functions ($\alpha_f = 1.093$, $\alpha_p = 1$) respectively on nitrogen and hydrogen does not change this result. This remark is quite important since it is well known [1,8,20,25] that the splitting between the first two vertical ionization potentials depends on the dihedral θ angle. For a C_2 structure, the two highest occupied molecular orbitals (MO) n_+ and n_- (5a, 4b) are nearly degenerate whatever the basis set used. So, it is thus deduced as observed experimentally, that the first two IPs are close (Table 2). At the MRSDQCI or CASPT2 level, the first ionization potential is well evaluated (9.80 ± 0.3 eV) while the second is generally lower than expected by about 0.4–0.5 eV (10.2 ± 0.3 eV against 10.64 eV experimentally). Moreover, from this analysis, we observe that whatever the extended atomic basis set used and the nature of the multiconfigurational wave functions, the calculated vertical IPs are constant. The broad threshold observed by Syage et al. from the photoionization efficiency curves for hydrazine indicates a large geometry change upon ionization, probably due to a modification of the dihedral angle θ. We have noticed the influence of the dihedral angle on the first two vertical ionization potentials.

Table 3
Optimized structural parameters for C_{2v}, C_{2h} and D_{2h} conformations of hydrazine ions $N_2H_4^+$ at the MCSCF level with TZP basis set. Bond lengths are in Å and angles in degrees. ΔE (eV) are the corresponding CASPT2 energies with reference to the N_2H_4 molecule

Structural parameters		C_{2v}		C_{2h}		D_{2h} [a]	
		$^2B_1$	$^2A_1$	^2A_g	^2B_u	$^2B_{2g}$	$^2B_{1u}$
$N_2H_4^+$	N_1N_2	1.325	1.707	1.319	1.742	1.318	1.646
	N_1H_1	1.002	1.016	0.999	1.009	0.999	1.000
	$N_1N_2H_1$	118.5	106.6	118.0	107.0	119.1	115.9
	$H_1N_1H_2$	121.0	108.4	120.5	115.5	121.8	128.2
	ΔE (eV)	7.78	11.88	7.64	12.08	7.67	12.49

[a] D_{2h} structure expected on ESR measurement [28,29].

The experimental splitting (≈ 0.6 eV) is only obtained for a variation of ten degrees on both sides of the equilibrium value ($90 \pm 1°$). We thus propose that a structural reorganization due to a modification of the dihedral angle is expected upon ionization with a very low ΔH^0 energy ($\leqslant 1$ kcal mol^{-1}). We have undertaken the calculations of the first two electronic states of the hydrazine ions under D_{2h}, C_{2v} and C_{2h} symmetry constraints. The fully optimized structures have been obtained from a MCSCF calculation with a TZP basis set. The electronic energies calculated at the CASPT2 level, for these structures, are reported in Table 3. As found earlier, it appears clearly that the ground state of $N_2H_4^+$ ion has C_{2h} symmetry, but the two other structures are very close and the $^2B_{2g}$ (D_{2h}) and ^2A_g (C_{2h}) electronic states are quasi-degenerate. The C_{2h} conformer is favoured by about 0.03 eV, which is similar to this earlier obtained by Pople et al. [10,26]. We found for the first adiabatic ionization potential ^1A (C_2) $\rightarrow$ ^2A_g (C_{2h}), at the CASPT2 level, a value (7.64 eV) (Table 3) weaker than this obtained by Pople and Curtiss [26] (8.07 ± 0.02 eV) using a G2 method which gives generally good ionization potentials, however, for the $N_2H_4^+$ ground state, the geometrical structure obtained in our work is the same. The incidence of the zero point vibrational energy correction (Table 4) on the first ionization potential seems weak (0.09 and 0.02 eV [6], respectively). The SCF calculations published by Nelsen et al. [27] underline that, if the semiempirical methods (INDO, MINDO) give the C_{2h} structure as the most stable for the $N_2H_4^+$ ion, the ab initio approach with a 6-31G basis set reverses this conclusion and gives the $^2B_{2g}$ (D_{2h}) state as favoured. In this work, we have calculated the harmonic vibrational frequencies of the quasi-degenerate ^2A_g (C_{2h}) and $^2B_{2g}$ (D_{2h}) ions, and also these of the fundamental state of N_2H_4 (^1A) with C_2 pyramidal gauche conformation. The D_{2h} structure appears as a saddle point with an imaginary frequency $\nu_{b_{2g}}$ (399 cm^{-1}). In fact, the double well ($C_{2h} \rightarrow D_{2h} \rightarrow C_{2h}$) is very flat and the first vibrational level is higher than the thermodynamic barrier.

3.2. Electronic spectrum

We have calculated the first excited singlet states between 5.75 and 13.3 eV. The vertical transitions

Table 4
Calculated harmonic vibrational frequencies (cm^{-1}) for gauche (C_2) conformation of N_2H_4 and for planar (D_{2h}) and (C_{2h}) $N_2H_4^+$ ions at the MP2 level. Zero point energy (ZPE) is calculated in eV

	N_2H_4 (C_2)			$N_2H_4^+$ (D_{2h})			$N_2H_4^+$ (C_{2h})	
	this work	[a]	exp. [b]		this work	[d]		this work
a	3673	3599	3310 [c]	a_g	3506	3766	a_g	3510
	3543	3486	3200 [c]		1697	1877		1704
	1718	1705	1628		1397	1570		1375
	1369	1376	1324	a_u	567	669	a_u	586
	1155	1167	1098	b_{1u}	3483	3732	b_u	3489
	875	898	780		1614	1765		1625
	446	401	377	b_{2g}	399i	208	a_g	169
b	3675	3585	3390	b_{2u}	3651	3898	a_u	3644
	3543	3474	3297		1037	1123		1039
	1707	1698	1587	b_{3g}	3633	3882	b_g	3631
	1332	1357	1283		1394	1527		1348
	1062	1101	937	b_{3u}	369	539	b_u	462
ZPE	1.49		1.41 [c]			1.52		1.40

[a] Ref. [30] calculated frequencies (cm^{-1}) using 6-31G* CI method. For other Hartree–Fock calculations of vibrational frequencies of N_2H_4 see [24,36–40].
[b] Ref. [30] which presents a critical analysis of several sources for assignments of vibrational frequencies of N_2H_4 by previous workers (see Refs. [30–35]).
[c] Ref. [34].
[d] Ref. [36]. Hartree–Fock (6-31G*) vibrational frequencies (cm^{-1}).

evaluated from the C_2 ground state $\tilde{\chi}$ (^{1}A) ($1a^2$ $1b^2$ $2a^2$ $2b^2$ $3a^2$ $3b^2$ $4a^2$ $4b^2$ $5a^2$) are all dipole allowed. For each transition, we have determined the oscillator strength. Moreover, for each state the total differential Mulliken population of the diffuse orbitals has been calculated. This population analysis is very useful for defining the dominant Rydberg or valence nature of the electronic states although this classification is rather arbitrary for a multiconfigurational description of the wave functions. In Table 5, we report the results obtained with a 6-31G* basis set including 3s 3p 3d 4s type of diffuse functions localized on the middle of the N–N bond. We first notice that the low lying states are all Rydberg states and the first valence state is only expected above 10 eV. According to Robin [13] for a pure Rydberg excitation, the oscillator strength does not exceed 0.08. Our Mulliken population analysis agrees with this intensity criterion. Moreover, our calculations do not predict any overlapping between Rydberg and valence $\sigma^* \leftarrow n$ transitions as assumed by Hopkirk [12] in order to explain the broad unstructured nature of the electronic spectrum of N_2D_4. On the other hand, our results imply that the $3d_R \leftarrow n_+$ and $3d_R \leftarrow n_-$ as well $4s_R \leftarrow n_+$ and $4s_R \leftarrow n_-$ are expected above 7.3 eV, much below the range where the first valence transitions appear (10.43 eV). Our results clearly indicate that below 10 eV only the first two Rydberg series occur: they correspond to the two series converging on the first and second IPs respectively. The first $2(^1A) \leftarrow \tilde{\chi}(^1A)$ transition is predicted to have a very low intensity ($f = 0.007$) at 5.75 eV

Table 5
Vertical transition energies of the low-lying excited states (C_2) and earlier assignments for the electronic spectrum of N_2H_4

Assignment	State		Transition type [a]	Rydberg pop. [b]	ΔE (eV) [c]	Te (eV)	f [d]
region I	2		5a → 3sa (ryd.)	0.80	5.75	4.02	0.007
	1	^{1}B	4b → 3sa (ryd.)	0.86	6.00	3.77	0.019
region II	2	^{1}B	5a → 3pb (ryd.)	0.89	6.79	2.98	0.010
	3	^{1}A	4b → 3pb (ryd.)	0.78	6.87	2.90	0.021
	3	^{1}B	5a → 3pb (ryd.)	0.94	7.33	2.44	0.033
	4	^{1}A	5a → 3pa, 3da (ryd.)	0.92	7.36	2.41	0.004
	5	^{1}A	4b → 3pb (ryd.)	0.94	7.39	2.38	0.006
	4	^{1}B	4b → 3da (ryd.)	0.95	7.54	2.23	0.006
	6	^{1}A	5a → 3pa,3da (ryd.)	0.95	7.87	1.90	0.004
	7	^{1}A	5a → 3da (ryd.)	0.96	8.06	1.71	0.001
region III	5	^{1}B	4b → 3da (ryd.)	0.96	8.12	1.65	0.004
	6	^{1}B	4b → 3pa, 3da (ryd.)	0.94	8.28	1.49	0.022
	7	^{1}B	5a → 3db (ryd.)	0.96	8.37	1.40	0.007
	8	^{1}B	4b → 3da (ryd.)	0.97	8.48	1.29	0.004
	8	^{1}A	4b → 3db (ryd.)	0.96	8.60	1.17	0.001
	9	^{1}A	5a → 3da (ryd.)	0.93	8.64	1.13	0.020
	10	^{1}A	5a → 4sa (ryd.)	0.92	8.79	0.98	0.000
	9	^{1}B	4b → 3da (ryd.)	0.97	8.83	0.94	0.001
	11	^{1}A	4b → 3da (ryd.)	0.98	9.03	0.74	0.003
	10	^{1}B	4b → 4sa, 3da (ryd.)	0.93	9.07	0.70	0.000
		^{2}A	5a	–	9.77	–	–
		^{2}B	4b	–	9.99	–	–
region IV	11	^{1}B	5a → val.	0.12	10.43	–	0.007
	12	^{1}A	5a → val.	0.26	10.62	–	0.001
	13	^{1}A	4b → val.	0.20	11.00	–	0.004
	12	^{1}B	4b → val.	0.09	11.24	–	0.093
	13	^{1}B	5a → val.	0.03	11.69	–	0.078

[a] Most important configurations in the multiconfigurational wave functions
[b] Total differential Mulliken population of diffuse orbitals
[c] Calculated energies relative to the ground state energy of N_2H_4 (MRSDQCI level)
[d] f: oscillator strength; $f = F|\mu|^2\nu$ with $F = 3.0375 \times 10^{-6}$ cm bohr^{-2}, μ (au) and ν (cm^{-1}).

(215 nm). This transition, essentially $3s_R \leftarrow 5a$, belongs to the first Rydberg series and is attributed to the poorly defined shoulder observed on the electronic spectrum at 5.69 eV enabling the term value determination at 4.02 eV. The second transition (6.00 eV) $1(^1B) \leftarrow \tilde{\chi}$ is more intense and corresponds to the relatively large band observed at 6.36 eV. The analysis of the multiconfigurational electronic wave function, as well as the study of the population analysis, both imply that the band is the first term of the second Rydberg series ($3s_R \leftarrow 4b$). The corresponding term value (3.77 eV) is obtained about 0.25 eV below the $3s_R$ term value of the first Rydberg series: this result corresponds to the energetical splitting of the first two IPs. Our propositions somewhat differ from those suggested by Robin, since on the electronic spectrum analysed by this author [3], the shoulder observed at 5.7 eV by Syage et al. [1] does not appear. Consequently, the $3s_R \leftarrow 5a$ transition was assigned by Robin to the intense band observed at 6.4 eV. On the other hand, the attribution proposed by Syage agrees with our analysis. Moreover, our results support the attributions proposed by Staemmler [11] and limited to the study of the first electronic 6a, 5b $\leftarrow n$ transitions (consisting mainly of the $3s_R$ AOs). Our study underlines that, in this region, the $3s_R$ and $3p_R$ Rydberg series should appear and that, beyond 7.5 eV, the $4s_R$ and $3d_R$ ones should be observed. Above the spectral zone where the two 3s Rydberg series occur, the transitions corresponding to the $3p_R \leftarrow 5a$ and $3p_R \leftarrow 4b$ series are expected. Our results clearly show that these transitions, and more particularly the first three, have a significant p Rydberg character. Up to 7 eV we observe a strong overlapping of $3p_R$ and $3d_R$ Rydberg characters and in addition it is difficult to distinguish the n_+ and n_- series as deduced from the multiconfigurational character of the wave functions. In this spectral zone, the strongest transition $3(^1B) \leftarrow \tilde{\chi}$ is calculated at 7.33 eV ($f = 0.033$) and can be attributed to the large unstructured band observed at 7.25 eV. This transition is essentially $3p_R \leftarrow 5a$ and the corresponding term value (2.44 eV) is very close to that proposed by Robin (2.68 eV) and Syage et al. (2.5 eV). The two $3p_R$ Rydberg transitions $2(^1B) \leftarrow \tilde{\chi}$ and $3(^1A) \leftarrow \tilde{\chi}$ expected to 6.79 and 6.87 eV respectively can be assigned to the shoulder observed on the previously mentioned band at 6.97 eV. In the next spectral zone, the experimental spectrum is poorly resolved, and it is not easy to attribute the calculated transitions which all belong to the $3d_R$ series. However the $6(^1B) \leftarrow \tilde{\chi}$, calcu-

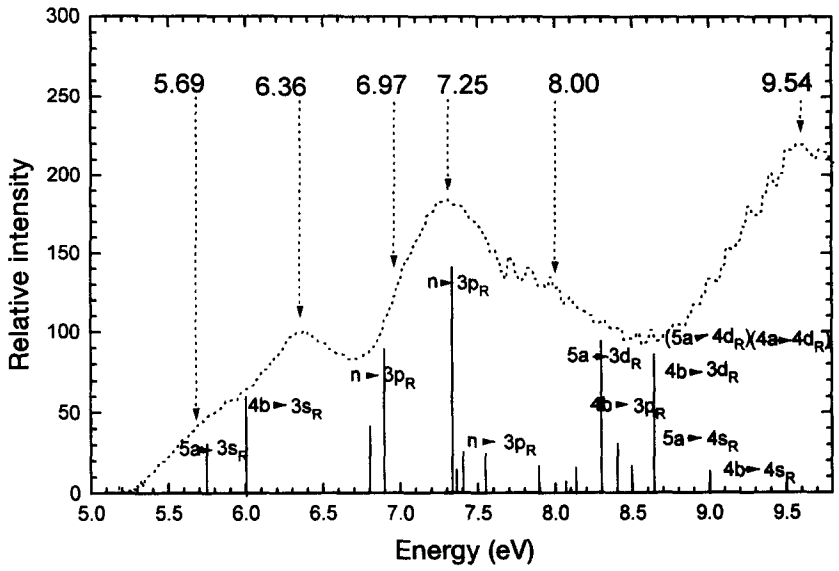


Fig. 1. Calculated Rydberg transitions at the MRSDCI level from 5.0 to 9.5 eV. The dashed lines represent the VUV electronic spectrum of hydrazine obtained by Syage et al. [1].

lated at 8.28 eV with a strong oscillator strength of (0.022) and a substantial contribution of $3p_R$ and $3d_R$ components, probably corresponds to the well defined shoulder observed at 8.27 eV. All the transitions which occur above 8.27 eV are predicted with a very low intensity, except the calculated one at 8.64 eV ($f = 0.020$). This can be considered to explain the very large and poorly resolved band beginning around 8.3 eV. The experimental spectrum of Syage et al. shows an important background which does not allow a detailed analysis of our theoretical results above 9 eV. The basis set of Rydberg orbitals used enables us to evaluate only the first Rydberg transition of each series, except for the s series. However, we assume that the $4d_R \leftarrow n$ transitions (term value less than 0.7 eV) should be found in the region between 9–10 eV. According to the value calculated for the $3d_R$ series for the quantum defect, we expect, as suggested by Syage, the $4d_R \leftarrow n$ transitions in a spectral region between 8.6 and 9.5 eV. These series converge on the first and second IPs. The valence transitions occur above the second ionization potential and the very strong valence transitions calculated respectively at 11.24 and 11.69 eV ($f = 0.093$ and 0.078) cannot appear in the spectrum obtained by Syage et al. All the results discussed above are summarized in Fig. 1 where we have reported the experimental data [1] and our theoretical results in the Rydberg transitions region from 5.0 to 9.5 eV.

As suggested by Syage et al. in order to understand the dynamic photorearrangement of N_2H_4, we have undertaken the calculation of the low-lying electronic states of hydrazine in a D_{2h} structure. The VUV absorption spectrum of hydrazine is broad and unstructured, what is generally attributed to a planarization of the Rydberg states in analogy with the $N_2H_4^+$ structure. The results obtained at the MP2 level (Fig. 2) underline that the low-lying electronic

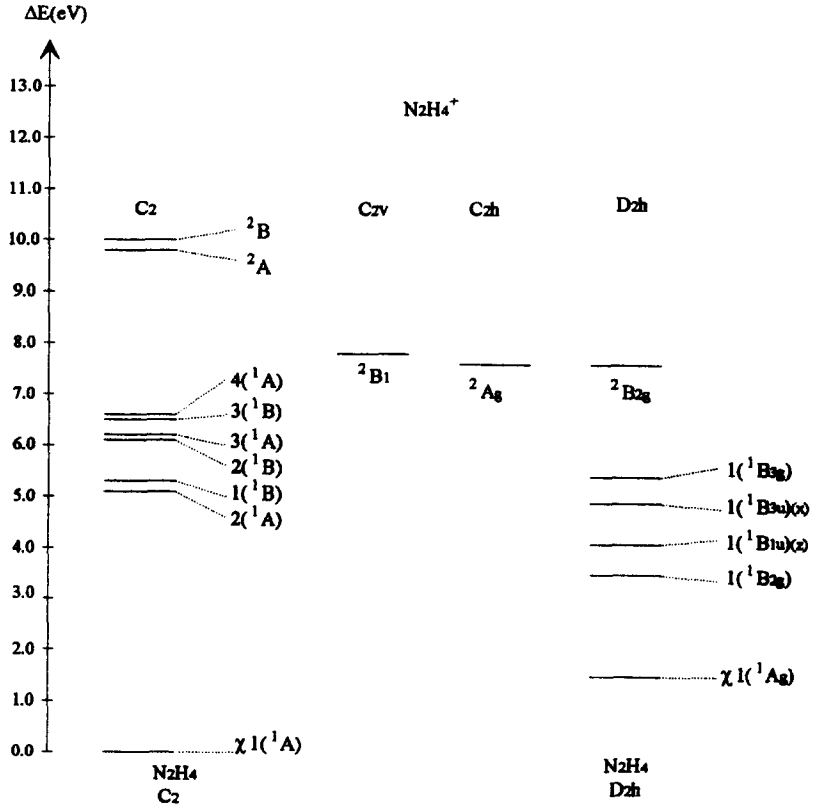


Fig. 2. Low lying electronic states calculated at the MP2 level with (6-31G* + diffuse Rydberg functions) basis set for N_2H_4 and $N_2H_4^+$ in C_2 and D_{2h} structure.

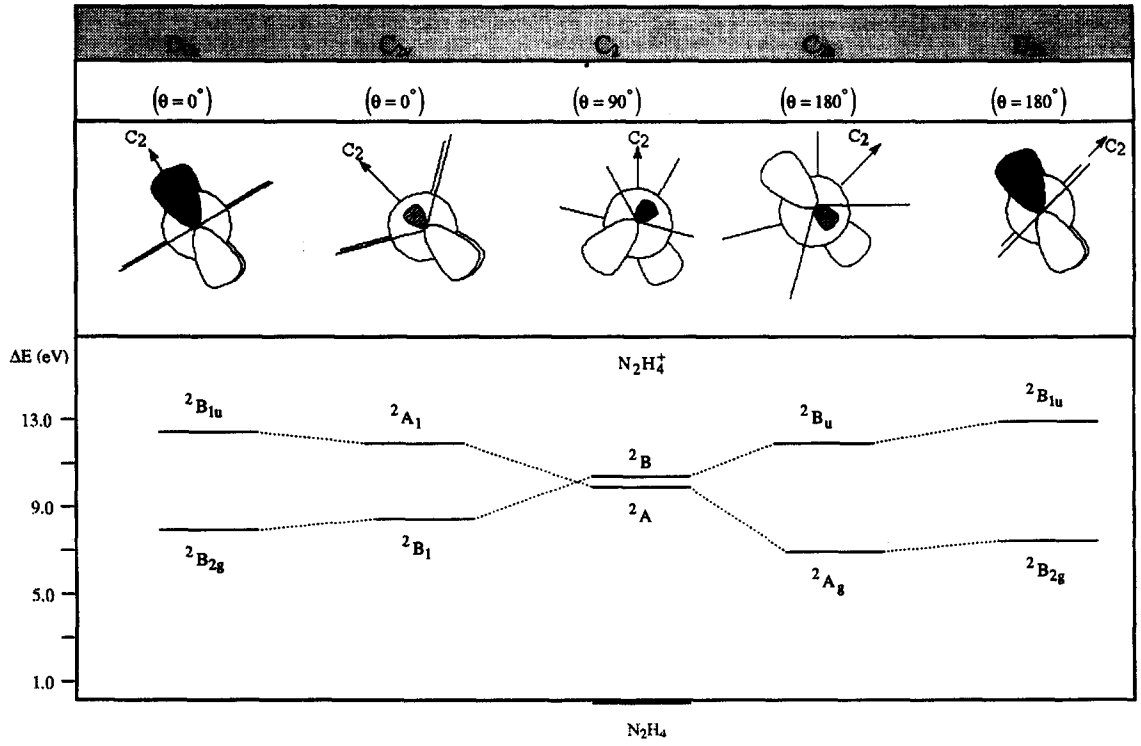


Fig. 3. Correlated electronic states for C_2, C_{2v}, C_{2h} and D_{2h} hydrazine ion conformations: scheme of interconversion from an internal rotation with preservation of the C_2 axis.

states are energetically more stable for the D_{2h} structure than for a C_2 one. We thus suggest that the second ^1A and first ^1B states (C_2) undergo without any thermodynamical barrier a conversion to the first $^1B_{2g}$ and $^1B_{1u}$ states (D_{2h}). The resulting stabilization energy from a C_2 to D_{2h} structure is about (1.6–1.8 eV) for the two states belonging to the first two Rydberg series. The energetical results concerning the first two electronic states of $N_2H_4^+$ are reported on Table 3. At the CASPT2 level, the ground state of $N_2H_4^+$ is the C_{2h} conformer (^2A_g) but the other structures (C_{2v} and D_{2h}) are very close, the energy differences being very small. We observe that from the two states ^2A and ^2B (C_2), an internal rotation of C_2 gauche conformation about the N–N bond, with preservation of one C_2 axis, would lead first to ^2A_g (C_{2h}) and $^2B1$ (C_{2v}) states, respectively (Fig. 3). The accuracy of the theoretical results (0.03 eV) does not allow to study the interconversion from C_{2v} to C_{2h} conformer which may occurs by a rotation about N–N bond or by a pyramidal inversion of the nitrogen atoms.

4. Conclusion

In the present study, ab initio calculations of the electronic states of hydrazine are presented and have enabled us to propose a detailed interpretation of the experimental spectrum. All the first electronic transitions appear as belonging to the first two Rydberg series without any overlapping with the valence transitions which are expected above 11 eV. This work includes a study of the first vertical and adiabatic IPs. The splitting between the first two vertical IPs is discussed and we propose that a structural reorganization is expected upon ionization. Moreover the first electronic states of hydrazine in D_{2h}, C_{2h} and C_{2v} structures have been calculated in order to contribute to the understanding of the dynamic photorearrangement.

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