Electronic Spectra of terraza tetrahedrane (N_4) isomers

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Abstract: RINDO/S calculation agumented by singly excited configuration interaction performed on the isomers of terrazatetrahedrane N_4. In this work we considered two isomers of N_4 which belong to D_{2h} and C_{2v} symmetry. These isomers are metastable and hence the interpretation of their spectra seems to be important. We report ionization potential, allowed singlet excitation, the triplet excitation and the singlet triplet splitting in each isomer. Rydberg excitations are also interpreted.

Key words: N_4 isomers, ionization potentials, electronic spectra.

INTRODUCTION

Metastability is a term usually assigned with a thermodynamically unstable form of some molecules that nevertheless, have a reasonable lifetime in that form. Molecules in electronic excited states that are probhited by selection rules from decaying to lower states via processes such as phosphor essence offer one example of metastability.

Another type which can term geometric metastabilty, is due to a particular arrangement of the atoms in a molecule. All molecules which can be formed in endothermic reactions are metastable relative to their simpler components, which mean they represent a local minimum on the potential energy surface which some other atomic arrangement constitutes the global minimum.

The potential existence of more exotic metastable species offers insight into the nature of the chemical bond. For example the normal form of phosphorus in P_4 while that of Nitrogen is N_2, although N_4 has the same qualitative valance bond description. is more stable than since has a relatively weak bond, while the bond is one of the strongest known. This does not indicate as a possible molecule but does imply that it is likely to be metastable [1].

Lauderdale et al [1] studied the bonding and stability of . They opine that synthesis of metastable molecules would offer a potential route towards the storage of large amount of energy. The evolving quest for more efficient explosive and rocket propellant has led to the examination of new and novel ways of strong energy [2].

In this work, we considered isomers to account for their electronic spectra. We hope that the results reported here would be helpful in further theoretical or experimental investigations. The method employed in the present work, can be found in reference [3].

The optimized geometries of isomers which were determined and characterized at the correlated level by Lauderdale et. al [1] were used in this work.

RESULTS

The Koopmans theorem [4] ionization potentials and the corresponding orbital symmetries are collected in Table 1. The lower singlet-singlet transition energies, oscillator strengths, and symmetries of the excited states are given in Table 2. The last column contains the percentages of Rydberg character of the excited states. The transition energies, the symmetries of the excited states, and the splitting of the eight lowest singlet-triplet transitions of both the isomers are cited in Table 3. the last columns give percentages of Rydberg Character of the states.

Table 1. The lowest ionization potentials of tetrazatetrahedrane (eV)

RIND O/S – CI

Molecule (symmetry)	I.P	Symmetry Of orbital	Type
N_4 (D_{2h})	11.07	b_{1u}	σ
	11.72	b_{1g}	π
	12.21	b_{3u}	σ
	14.76	A_g	σ
	14.96	b_{2u}	π
	17.74	A_g	σ
	18.07	b_{2g}	σ
	24.64	b_{1u}	σ
	29.08	b_{3u}	σ
	42.07	A_g	σ
N_4 (C_{2v})	10.11	b_2	σ
	11.68	b_1	π
	14.47	a_1	σ
	15.03	a_1	σ
	15.27	a_1	σ
	15.72	a_1	π
	20.57	a_1	σ
	23.37	b_2	σ
	32.05	a_1	σ
	40.86	a_1	σ

Table 2. Lowest singlet-singlet transitions in N4. All energies are in eV

Molecule (Symmetry)	Transition Energy	RIND O/S F	Symmetry of Excited state	Type	% Rydberg Character N
N_4 (D_{2h})	1.33	0.000	b_{2u}	n→π*	0
	2.39	0.000	A_u	n→π*	0
	2.81	0.000	b_2g	n→π*	0
	2.87	0.000	b_{1g}	n→π*	0
	3.67	0.000	b_{3g}	n→π*	0
	5.00	0.035	b_{1g}	n→π*	0
	5.58	0.000	b_{3g}	n→π*	0
	5.97	0.000	b_{1g}	n→σ*	0
	6.06	0.000	b_{2g}	n→σ*	0
	6.08	0.000	b_{2u}	n→σ*	0
	6.38	0.019	b_{1u}	n→σ*	0
	6.69	0.000	a_g	n→σ*	0
	6.75	0.083	b_{3u}	n→σ*	5
	6.86	0.000	a_u	n→π*	0
	7.86	2×10^{-6}	a_g	n→σ*	3
	7.90	0.000	b_{3g}	n→π*	2
	7.92	0.015	b_{1u}	n→σR*	96
	8.18	0.000	b_{2g}	n→π*	0
	8.22	0.191	b_{3g}	n→σ*	13
	8.23	0.458	b_{1u}	n→π*	4
	8.25	0.000	b_{3g}	n→σ*	11
	8.37	0.000	a_u	n→σ*	2
	8.57	0.000	b_{1g}	n→σ*	100
	8.72	0.000	b_{2g}	n→σ*	100
	8.76	0.000	a_g	n→σ*	99
	8.99	0.000	b_{3g}	n→σ*	100
	9.04	0.002	b_{3u}	n→σ*	99
	9.18	0.000	b_{1g}	n→σ*	0
	9.30	3×10^{-4}	b_{3u}	n→σ*	92
N_4 (C_{2u})	1.00	0.000	a_2	n→π*	0
	2.49	0.006	b_2	n→σ*	0
	2.48	0.000	a_2	n→π*	0
	3.48	0.034	b_2	n→π*	0
	4.04	0.003	a_1	n→σ*	0
	4.38	0.000	b_1	n→σ*	0
	4.56	0.000	a_2	n→σ*	0
	5.40	0.000	a_2	n→π*	0
	5.62	0.000	a_2	n→π*	0
	5.75	0.113	a_1	n→π*	0
	6.50	0.000	b_1	n→π*	0
	6.59	0.052	b_2	n→π*	1
	6.68	0.000	a_2	n→σ*	1
	6.77	0.081	a_1	n→σ*	1
	6.88	3×10^{-4}	b_2	n→σ*	99
	7.13	0.000	b_1	n→π*	0
	7.65	0.000	b_2	n→σ*	100

7.85	0.000	b_1	n→σ*	0
7.93	0.000	a_2	n→σ*	100
7.94	1x10⁻⁴	a_1	n→σ*	99
8.13	8x10⁻⁴	b_2	n→σ*	96
8.14	0.023	b_2	n→σ*	4
8.26	0.000	b_1	n→σ*	100
8.43	0.000	a_2	n→σ*	0
8.53	0.012	a_1	n→σ*	97
8.54	0.000	a_2	n→σ*	100
8.68	0.435	a_1	n→σ*	6
8.78	0.074	b_2	n→σ*	97
9.14	0.203	b_1	n→σ*	1

Table 3. the eight lowest singlet-triplet transition in N4 energies are in eV

Molecule (Symmetry)	RIND O/S Transition Energy	S-T Split	% Rydberg Character Symmetry of excited State	Type	N
N_4 (D_{2h})	0.60	2.21	b_{2g}	n→π*	0
	0.87	0.46	b_{2u}	n→π*	0
	1.61	0.78	a_u	n→π*	0
	1.63	3.37	b_{1u}	n→π*	0
	2.34	0.53	b_{1g}	n→π*	0
	2.61	1.06	b_{2g}	n→π*	0
	4.80	1.95	b_{3u}	n→σ*	0
	4.89	1.17	b_{2g}	n→σ*	0
N_4 (C_{2u})	0.62	0.36	b_1	n→π*	0
	2.25	0.24	b_2	n→π*	0
	2.44	0.98	a_2	n→π*	0
	2.86	2.89	a_1	n→π*	0
	3.35	0.69	b_1	n→σ*	0
	3.77	0.61	b_1	n→σ*	0
	4.18	0.38	a_2	n→σ*	0
	4.93	0.47	a_2	n→π*	0

3. DISCUSSION

3.1 Ionization potentials

The first ionization potential of both the isomers is interpreted as the removal of an electron from in-plane s orbital while the second one as the removal of an electron from an out-of-plane p orbital. It is worthwhile to notice that the first s electron to be removed from C_{2v} N_4 requires less energy than that from D_{2h} N_4 while the second s electron to be removed from C_{2v} N_4 requires much more energy than that from D_{2h} N_4. Again the last electron to be removed from C_{2v} N_4 requires less energy (40.86 eV) than that from D_{2h} N_4 (42.07 eV). Thus we find no definite trend of variation in Ionization Potentials of the isomers.

a.   Singlet excitations

(i) D_{2h} N_4.

The present calculations predict the most of the low lying singlet – singlet and singlet – triplet transitions in D_{2h} N_4 are almost entirely valance shell transitions. The contribution of Rydberg orbitals to some excited states is moderate but much stronger Rydberg contributions come into play at higher energies. This is also true in C_{2h} N_4. The first absorption in D_{2h} N_4 occurs at about 5.00ev. The transition corresponding to this absorption is assigned as n®p* which has an oscillator strength amounting to 0.035. The maximum absorption in D_{2h} N_4 occurs at about 8.23ev. The transition corresponding to the maximum absorption is assigned as n®p* which has an oscillator strength amounting to 0.458. The spectrum of D_{2h} N_4 consists of ns and np Rydberg series converging upon the first ionization potential at 11.07 ev.

b.   Triplet Excitations

As mentioned above, the spectra of N_4 isomers are devoid of p-p states and hence question of the separations of the lowest single -p and n-p states does not arise. The allowed n®p* transitions exhibit intensity. The separations between the lowest singlet and triplet n-p states are as follows. This is about 2.21eV in D_{2h} N_6 and 0.36eV in C_{2V} N_4. It is noteworthy that the first intense singlet n®p* transition in D_{2h} N_4 at 5.00eV is separated by the corresponding triplet by a large amount of energy (3.37eV). A similar situation in C_{2V} N_4 is found for the triplet state at 2.86eV. It is noteworthy that the splits calculated for the n®s* transitions in D_{2h} N_4 are much larger than that in C_{2V} N_4.

CONCLUSION

The electronic spectra of the isomers have not yet been observed or theoretically calculated. The ground as well as the excited state properties reported here will be forthcoming. The structural features of the spectra of the isomers are well

pronounced under the present calculation. We hope that the present results would be helpful in further studies.

References

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