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The electronic states of 1,2,5-thiadiazole studied by VUV absorption spectroscopy and *ab initio* configuration interaction methods

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Abstract

The 1,2,5-thiadiazole VUV absorption spectrum over the range 5–12 eV has been obtained for the first time. It shows broad bands centred near 5.0, 7.2, 7.7, 8.7, 9.6 and 10.6 eV; several of these show well resolved vibrational structure. A number of valence states and Rydberg states relating to the first and second ionisation energies have been identified. The doubling of some bands in the 4.7 eV region (previously reported) is confirmed; a 3s Rydberg state shows a similar phenomenon, which we also attribute to a non-planar upper state; a study of the (planar) equilibrium geometry of the corresponding triplet Rydberg state shows it is a saddle point. Electronic excitation energies for valence (singlet and triplet) and Rydberg-type states have been computed using *ab initio* multi-reference multi-root CI methods. These studies used a triple-zeta + double polarisation basis set, augmented by diffuse (Rydberg) orbitals. The theoretical study shows the nature of the more intense Rydberg state types, and positions of the main valence and Rydberg bands. There is generally a good correlation between the theoretical intensities and the experimental envelope. Reconsideration of the order of cationic states in the UV-photoelectron spectrum, crucial to the Rydberg state interpretation, has led to the sequence: $^2B_1 < {}^2B_2 < {}^2A_2 < {}^2A_1$. Study of the excitation energies to specific upper states, also supports this order. The value of IE_1 is refined to 10.111 eV. Equilibrium structures show the π- and σ-cations are planar, in contrast to the lowest triplet state.

Keywords: VUV spectrum; CI calculations; Photoelectron spectrum; Singlet states; Triplet states; Ionic states

1. Introduction

Ultraviolet (UV) spectroscopy has proved to be one of the most difficult forms of spectroscopy for detailed interpretation, owing to the major computational requirements. This is especially true where differing excitation processes are possible. We have previously reported a series of joint experimental and theoretical studies of the UV + vacuum-UV (VUV) spectra of the five-membered ring sulphur containing heterocycles shown in Fig. 1, including thiophene (**1**) [1,2], isothiazole (**2**) [3] and thiazole (**3**) [4].

We now report a study of the combined UV + VUV spectrum of 1,2,5-thiadiazole (**4**), together with a large scale CI study of the electronically excited (singlet and triplet) valence and Rydberg states. Because of initial problems with Rydberg state assignments, we have also reinvestigated the order of cationic states in the UV-photoelectron spectrum (UV-PES) [5], since this is fundamental to determination of the sequence of Rydberg states. A significant reassignment of the UV-PES is presented.

Previous spectroscopy of 1,2,5-thiadiazole is limited to a few lines in the first band of the UV spectrum although the spectrum itself was not displayed [6]. These lines were analysed in terms of a double-potential minimum for a non-planar excited state. Three vibrations were identified, and compared with the ground state values. Similar brief studies on 1,2,5-oxadiazole and -selenadiazole [7,8] have been reported. The UV spectrum is part of the present UV + VUV combined study.

This ring system is rare in nature [9], but recently amino acid derivatives of 1,2,5-thiadiazol-3-yl-piperazine have

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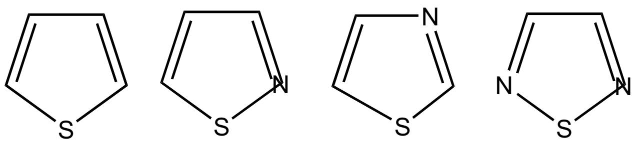

1,thiophene 2, isothiazole 3, thiazole 1,2,5-thiadiazole

Fig. 1. The S-azole series of molecules.

been shown to be important in mood control [10] as examples of non-benzodiazepine anxiolytics; other uses are in possible treatment of Alzheimer's disease [11], and as antibacterial and anti-fungal agents (sulphametrole) [12].

1.1. Electronic structure of the ground state of 1,2,5-thiadiazole

The doubly occupied SCF orbitals for the $\widetilde{X}^1A_1$ ground state (C_{2V} symmetry) [5] are $1a_1$–$11a_1$ and $1b_2$–$7b_2$ (all σ-electrons), $1b_1$–$3b_1$ and $1a_2$ (π-electrons). Conventionally, there is a 'lone pair' on S (LP_S), and one on each N atom (LP_N), although the latter occur as linear combinations, LP_N^+ and LP_N^-. These LP MOs are far from localised on the S and N atoms; Mulliken analyses of these are shown in Table 1; non-integral sums indicate residues on the C + H atoms. Whilst $7b_2$ is largely localised on N, and hence is reasonably designated as LP_N^-, the $11a_1$ and $10a_1$ MOs are clearly mixtures of LP_N^+ and LP_S.

The combined symmetry sequence is discussed in relation to the UV-PES below. In all the CI results described here for 1,2,5-thiadiazole, the 9 core MOs (1–$5a_1$, 1–$3b_2$, $1b_1$) are frozen at 2.0e for each MO.

1.2. Molecular structure of 1,2,5-thiadiazole

The ground state rotational (A, B, C) and quartic centrifugal distortion constants, have been determined by microwave [13,14] and high resolution infrared spectral (IR) studies [15], respectively. An electron diffraction (ED) study [16] has also been reported. These structures, as well as our ground state structure are all relatively similar.

1.2.1. Assignment of the ionisation energies ($IE_{V,A}$) from the UV-PES spectrum

A UV-PES study of 1,2,5-thiadiazole [5], gave an assignment of ionisation energies (IE) based upon orbital energies (Koopmans' Theorem, where $IE_i = -\varepsilon_i$); the calculated order of the lowest IE's were $3b_1^{-1} < 1a_2^{-1} < 7b_2^{-1} < 11a_1^{-1} \ll 10a_1^{-1} < 6b_2^{-1} < 2b_1^{-1}$. Several IE were well resolved with IE_A (adiabatic) 10.145 (IE_1), 10.84 (IE_2) 13.67 (IE_5) and 13.92 (IE_6) eV [5]. *IE_1* showed a complex vibrational progression of at least 8 members; the strong 0–0 band (where the adiabatic (IE_A^1) and vertical (IE_V^1) ionisation energy coincide) implied a π-ionisation (π_4^{-1}) [1–5]. The new Rydberg state results (below) show that a small refinement of IE_1 to 10.111 eV is required. Both IE_2 and IE_6 have Gaussian-type envelopes; although IE_2 and IE_3 overlap, identification of IE_A^2 is possible. The fine structure on IE_3 and IE_4 is insufficient to determine IE_A [5], so that IE_V must suffice for that band in the present study. To assist discussion below, the UV-PES together with its new assignment (Section 4.2.2, and Table 3) is shown in Fig. 2.

The Rydberg formula is $IE_A - E = R/(n - \delta)^2$, where R is the Rydberg constant (13.606 eV), n is the principal quantum of the upper (Rydberg) orbital, and δ is the quantum defect. The four IE_A^x (where $x = 1, 2, 5, 6$) above, should show Rydberg 3s states (for $n = 3$, $\delta = \sim 1$) below an energy of 11 eV, so all of these IE, as well as IE_2 and IE_3 will contribute to the VUV envelope in the present range below 12 eV. Absorption bands arising from excitation of a pure Rydberg state are expected to exhibit the vibrational structure of the UV-PES, and were identified by this process.

2. Experimental study

A full description of the experimental procedure, supplied by the Daresbury Laboratory, where the measurements were performed, was reproduced previously [3,4].

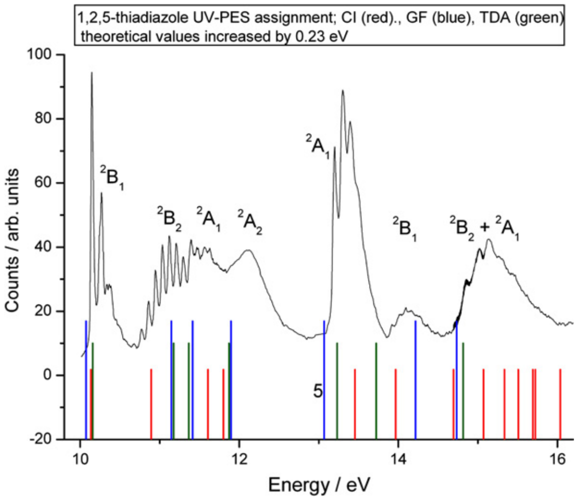

Fig. 2. The UV-PES spectrum and revised assignment.

Table 1
Mulliken analyses of the 'lone pair' orbitals at the SCF level

SCF-MO	Symmetry	Type	S_1			$N_2 + N_5$		
			s	p	d	s	p	d
20	$7b_2$	LP_N^-	0.0	0.0716	0.0137	0.0914	0.7537	0.0006
19	$11a_1$	LP_N^+	0.0101	0.3000	0.0038	0.0446	0.3200	0.0022
18	$10a_1$	LP_S	0.1454	0.2110	0.0141	0.1080	0.3400	0.0022