



A study of the electronic states of pyrimidine by electron energy loss spectroscopy



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ABSTRACT

The electron energy loss spectra were measured in pyrimidine at the constant electron residual energy varied from 15 meV to 10 eV and in the scattering angle range 0–180°. The spectra were analysed applying an iteration fitting procedure to resolve the energy loss bands corresponding to excitation of the electronic states of pyrimidine. The vertical excitation energies of the singlet states of pyrimidine and of a number of the triplet states were determined. The presently observed triplet states were tentatively assigned.

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1. Introduction

The electron energy loss spectroscopy is a powerful technique in the studies of the excited states of polyatomic molecules, providing important complementary spectroscopic data to that obtained from photoabsorption spectra. It was experimentally confirmed that performing the combined variable scattering angle and the residual electron energy measurements differentiation between and identification of the optically-allowed and -forbidden transitions could be achieved [1,2]. Here, at small scattering angles and a high residual electron energy (>10 eV) the excitation of the optically-allowed states dominates the energy loss spectra, while at the lower residual electron energy (<3 eV) and large scattering angles the relative intensity of the optically-forbidden transitions increase. In particular, the scattering at 180° should be governed by the electron exchange interaction which favours singlet–triplet excitation. Moreover, the spin- and symmetry-forbidden transitions usually dominate in the near-threshold spectra measured at low residual electron energy. It has also been pointed out on the ground of group theoretical considerations that in the symmetry-forbidden transitions the differential excitation cross section at 0° and 180° (electron axial scattering) should be zero for diatomic molecules and relatively low for polyatomic molecules [3].

The present work aims to provide new data on the excited states of pyrimidine by measuring and analyzing the electron energy loss spectra obtained at the constant residual electron energy varied from 15 meV to 10 eV and at the selected scattering angles from 0° to 180°. Pyrimidine (1,3-diazine), C₄H₄N₂, belongs to azabenzenes,

a group of molecules that are isoelectronic with benzene (C₆H₆). It has a planar ring geometry incorporating two nitrogen heteroatoms at positions 1 and 3 and belongs to the C_{2v} point group in the electronic ground state. In comparison with benzene, replacement of two C–H groups with nitrogen atoms in the benzene ring shifts the energy levels to higher values and gives rise to new transitions due to excitation of nitrogen lone pair electrons from the non-bonding (n_N) orbitals. The relatively simple pyrimidine molecule is often considered as a molecular model of the pyrimidine nucleic acids (thymine, cytosine) and thus has recently gained an increased interest in the studies of interaction and damage induced by ionizing radiation in the biological matter [4].

The electronic configuration of the outermost molecular valence orbitals of the \tilde{X}^1A_1 ground state of pyrimidine may be written as ... (1a₂)²(11a₁)²(2b₁)²(7b₂)² [5,6], while the lowest unoccupied molecular orbitals are (2a₂)(3b₁)(12a₁)(4b₁) [6,7]. The 11a₁ and 7b₂ orbitals have been identified as the non-bonding (n_N) orbitals, while the 1a₂, 2b₁ and the unoccupied 2a₂ and 3b₁ orbitals as having π character [5]. Consequently, in the low energy range the pyrimidine excitation spectrum will contain bands corresponding to the n_Nπ* and ππ* states of the A₂, B₁ and A₁, B₂ symmetries, respectively. However, it is worth noting, as demonstrated by the calculations [5], that some of the excited states of pyrimidine have to be described by taking into account the configuration interaction and vibronic coupling.

The excited electronic states of pyrimidine in the 3.5–11 eV energy range have been assigned in the photoabsorption measurements [5,6,8,10,11]. Some earlier works have been critically reviewed in Ref. [12]. The photoabsorption spectrum of pyrimidine contains three distinct broad bands at 5.2, 6.7 and 7.5 eV, which are accompanied by two lower intensity bands at 4.2 and 8.9 eV. These bands were assigned to the ¹B₂, ¹A₁, ¹A₁ and ¹B₂,

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1B_1 singlet states, respectively. Some of the bands show superimposed vibrational structure of the excited Rydberg states. There is much less spectroscopic data on the triplet states and symmetry-forbidden transitions in pyrimidine. The lowest lying 3B_1 triplet state of pyrimidine has been firmly located by observing laser-induced phosphorescence bands, which have an origin at 3.538 eV [13,14]. To observe the triplet states at higher energies the near-threshold electron energy loss spectra were measured using the trapped electron technique [9,10]. The rather weak features in the excitation spectrum of Ref. [10] were assigned with an aid of the multi-reference configuration interaction calculations, but were reassigned in Ref. [11]. The electron energy loss spectra have been recently obtained for the impact energies of 15–50 eV and the scattering angle range 10–90° in the measurements of the differential cross sections [15,16]. Six excitation bands of unresolved valence singlet and triplet states have been recorded in the energy range from 3 to 10 eV. High impact energy (150 eV) energy loss spectrum was also reported previously [17]. Apart from the above gas phase studies, the electronic excitation of pyrimidine have been equally investigated for the three-layer films deposited on solid argon in the low incident energy range 2–12 eV [18]. In this study, the main features below 7 eV in the energy loss spectra were ascribed to the triplet states.

A number of theoretical calculations on the electronic states of pyrimidine, which applied *ab initio* and density functional approaches have been also performed [5,10,11,19–24]. These works deliver rather more results on the spectroscopy of the singlet than the triplet states. A fair consistency has been achieved for the singlet states between different theoretical approaches and the experiment.

2. Experimental details

The electron energy loss spectra in pyrimidine were measured employing electron spectrometer that has been described in detail in our previous publication [25]. It consists of a source of energy-selected electrons, a capillary to produce the target gas beam and a scattered electron analyzer that can be rotated around the axis of the gas beam. It also incorporates a magnetic angle changer [26] to extend the scattering angle range from 90° to 180°. The electron analyzer was equipped with an extracting electrode [27] to implement a penetrating electrostatic field technique [28] for the measurements of the threshold energy loss spectra. The electron spectrometer is also furnished with a magnetic field deflector placed between the exit of the hemispherical selector in the electron analyzer and the electron channel multiplier [27]. It was used to estimate the possible contribution of low kinetic energy negative ions into the threshold electron spectra. Such contributions, if present, were below 5% of the scattered electron intensity.

All spectra recorded were measured in the mode of the constant residual electron energy E_R . At E_R energies between 2 and 10 eV the scattered electrons were collected at a fixed scattering angle. In the threshold mode of operation of the analyzer ($E_R < 0.15$ eV), electrons were collected from a larger solid angle (up to 4π) of the scattering region. The energy loss spectra were measured with an energy resolution of 60–80 meV (FWHM). The electron energy loss scale in the non-threshold mode was determined against the elastic scattering peak with an uncertainty of ± 5 meV. In the threshold mode, the electron energy loss was calibrated against the position of the 2^1S excitation peak in helium to within ± 5 meV, by measuring the threshold spectra in mixture with pyrimidine. In this mode, the E_R energy was estimated from the intensity ratio of the 2^1S to 2^3S threshold peaks [29].

The scattering angle Θ was calibrated against known positions of minima in the elastic electron scattering in argon with an

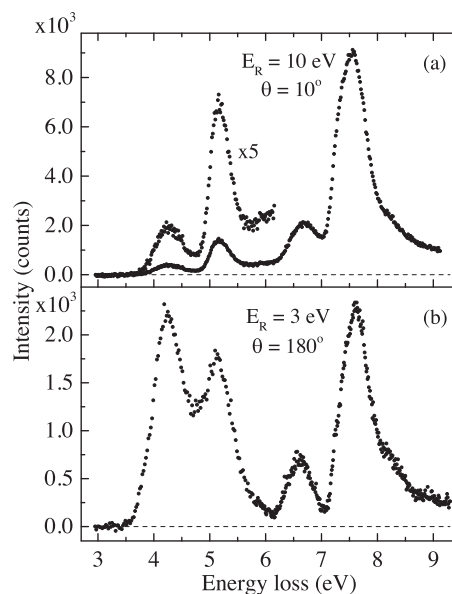


Figure 1. Electron energy loss spectra measured in pyrimidine for the constant residual energy E_R and the scattering angle Θ : (a) 10 eV and 10°, (b) 3 eV and 180°.

uncertainty of $\pm 1.5^\circ$. However, in the measurements with the magnetic angle changer, the angular uncertainty was higher, for example $\pm 3^\circ$ at 180°. This was caused by the energy dependence on the deflection of the incident electron beam in the magnetic field. To minimize this effect, the energy loss spectra at 180° were measured in the shorter energy ranges and the obtained spectra were combined into a final spectrum. To aid the angular calibration, the electron trajectories in the magnetic field were simulated using CPO computer program [30].

The liquid pyrimidine with a stated purity of 98% was purchased from Sigma–Aldrich. The sample was kept in a stainless steel container heated to approximately 40 °C. The pyrimidine vapour was introduced into the spectrometer by a gas line kept at 50 °C, while the apparatus was at 60 °C. The pyrimidine in the container was degassed several times under low pressure.

3. Results

The electron energy loss spectra measured in pyrimidine at $E_R = 10$ eV, $\Theta = 10^\circ$ and $E_R = 3$ eV, $\Theta = 180^\circ$ are presented in Figure 1a and b, respectively. The (a) spectrum displaying energy loss bands at 4.2, 5.2, 6.7 and 7.6 eV resembles well that of the VUV photoabsorption measurements [6]. Although its relative band intensities differ from those of the VUV spectrum, both spectra demonstrate the highest intensity band at 7.6 eV. The shape of the present spectrum is also in accord with that measured previously in Refs. [16,17] at electron energy of 50 and 150 eV, respectively. The (b) spectrum obtained at lower E_R energy and backward scattering shows increased intensities of the energy loss bands at 4.2 and 5.2 eV together with a slightly lower width of the 7.6 eV band. A detailed comparison of the (a) and (b) spectra reveals differences in the positions of the maxima in the 5.2 and 6.7 eV bands. The shift of the maxima and the variation of the shapes and widths of the 5.2 eV energy loss band are clearly demonstrated in Figure 2, which compares two threshold spectra measured at $E_R = 15$ and 140 meV with an energy loss spectrum of $E_R = 10$ eV and $\Theta = 30^\circ$. For example, the maximum in the $E_R = 140$ meV spectrum appears 60 meV below that of the $E_R = 10$ eV spectrum. The increased widths and variation of the shapes of the bands in the threshold spectra undoubtedly indicate the excitation of several pyrimidine states in this energy

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