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ScienceDirect
Chemical Physics 344 (2008) 227–236
Chemical Physics
www.elsevier.com/locate/chemphys

The valence shell electronic states of ethylene sulphide studied by photoabsorption and ab initio multireference configuration interaction calculations

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Received 21 November 2007; accepted 4 January 2008
Available online 10 January 2008

Abstract

The absolute photoabsorption cross section of ethylene sulphide has been measured between threshold and 30 eV using monochromated synchrotron radiation. Below the ionisation threshold the spectrum exhibits numerous sharp peaks associated with Rydberg states belonging to series converging onto the $\widetilde{X}^2B_1$ limit. At excitation energies above the ionisation threshold at 9 eV intravalence transitions play a dominant role, resulting in the appearance of prominent broad bands. Much weaker structure ascribed to Rydberg states associated with excitation from the $4b_2$, $8a_1$ or $2b_1$ orbitals is also discernible. Ab initio multireference configuration interaction calculations have been performed to obtain excitation energies for valence electron transitions into Rydberg or virtual valence orbitals. These theoretical predictions have enabled assignments to be proposed for most of the structure due to Rydberg series converging onto the $\widetilde{X}^2B_1$ limit. The calculations show that configuration interaction is important in the description of many of the excited states.

Keywords: Photoabsorption; Rydberg and valence states; Ab initio multireference configuration interaction calculations

1. Introduction

The three-membered ring molecules cyclopropane, ethylene oxide and ethylene sulphide constitute excellent candidates for studying the way in which electronic properties depend on chemical bonding and geometric structure. These molecules are sufficiently small for their electronic and geometric structures to be treated realistically by ab initio methods, and the results obtained from such calculations can be used to generate photoabsorption and photoelectron spectra. By comparing the measured absolute photoabsorption cross sections for cyclopropane, ethylene oxide and ethylene sulphide with predicted transition energies and oscillator strengths, the contributions from Rydberg excitations can be distinguished from those of intravalence transitions. This, in turn, allows Rydberg/valence mixing in these molecules to be evaluated. Another issue to be addressed is the nature of the excited state: can it be approximated by a single dominant configuration or must configuration interaction be taken into account? Recently we have investigated the valence shell electronic states of cyclopropane through VUV absorption measurements and ab initio multireference configuration interaction calculations, and obtained a satisfactory understanding of the electronic properties [1]. The present work describes a similar study on ethylene sulphide (also known as thiirane). This molecule exhibits a far more complicated photoabsorption spectrum which can be explained only through the inclusion of extensive configuration interaction in the description of the excited states.

To some extent the photoabsorption spectra of cyclopropane (C_3H_6), ethylene oxide (C_2H_4O) and ethylene sulphide (C_2H_4S) are similar, displaying sharp structure, due

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doi:10.1016/j.chemphys.2008.01.006

to excitation from the outermost orbital, below the ionisation threshold followed by a region of continuous absorption. These continuum regions contain prominent broad features associated with intravalence transitions together with weaker structure ascribed to Rydberg excitations from the more tightly bound valence orbitals. Above their respective ionisation thresholds, the absorption spectra of these three molecules have much in common. However, below the ionisation threshold the structure due to Rydberg transitions is relatively weak and simple to interpret in cyclopropane [1], becomes more extensive in ethylene oxide [2] and is complex in ethylene sulphide.

The most comprehensive investigation of the Rydberg series converging onto the ground state ionisation threshold of ethylene sulphide is the two- and three-photon resonance enhanced multiphoton ionisation study performed by Morgan et al. [3]. In that work, six dipole allowed Rydberg series associated with excitation from the outermost orbital into s-, p- or d-type orbitals were identified and compared with results from earlier single photon measurements [4–8]. Their analysis suggested that, as in H_2S [9], many of the Rydberg orbitals in ethylene sulphide possess hybrid l character, where l is the orbital angular momentum. This mixing between angular momentum components is confirmed in the present calculations. Whereas in cyclopropane the upper state could be described reliably in terms of a single configuration, this is not the case for valence shell transitions in ethylene sulphide.

According to the present calculations, the ground state ($\widetilde{X}^1A_1$) electronic configuration of ethylene sulphide, in C_{2v} symmetry, may be written as

core/inner shell $(1a_1)^2\ (2a_1)^2\ (1b_2)^2\ (3a_1)^2\ (4a_1)^2\ (2b_2)^2\ (1b_1)^2$,
valence shell $(5a_1)^2\ (3b_2)^2\ (6a_1)^2\ (2b_1)^2\ (7a_1)^2\ (1a_2)^2\ (8a_1)^2\ (4b_2)^2\ (3b_1)^2$.

In this nomenclature, the z-axis corresponds to the C_2 axis and the heavy atom ring lies in the yz plane. The HeI [10–12] and HeII [11] excited photoelectron spectra of ethylene sulphide exhibit six bands having vertical ionisation energies less than 17 eV, due to ionisation from the six outermost orbitals. A short vibrational progression, with a peak to peak spacing of ~130 meV, is observed in the $\widetilde{X}^2B_1$ state photoelectron band. The threshold photoelectron spectrum has also been recorded and displays similar features [13]. Recently the vibrational structures of ground state ethylene sulphide ions have been studied using mass analysed threshold ionisation spectroscopy and have been interpreted with the aid of ab initio calculations [14].

2. Experimental apparatus and procedure

The absolute photoabsorption cross section of ethylene sulphide was measured using two experimental chambers – a cell incorporating LiF windows, and a windowless double ion chamber [15] – and synchrotron radiation emitted from the Daresbury Laboratory storage ring. In both cases the experimental chamber was attached to a 5 m normal incidence monochromator, which delivers radiation over the photon energy range of 5–40 eV, and has been described in detail previously [16]. In the present experiment a photon resolution of 0.1 nm FWHM (~5 meV at $h\nu = 8$ eV) was employed.

Each of the LiF windows defining the absorption cell was mounted within a gate valve, and the distance between the windows was 25.6 cm. After passing through the second of these windows, the radiation entered an evacuated region, of length ~25 cm, before impinging upon a sodium salicylate screen sprayed upon a glass window. The resulting fluorescence passed through a blue Kodak Wratten 47B filter, to remove the long wavelength scattered light, before being detected with a photomultiplier. The glass window formed the vacuum/air interface. The purpose of the evacuated region was to separate the gas sample from the sodium salicylate screen, thereby ensuring that the fluorescence efficiency was not affected by surface reactions.

The gas entered the absorption cell through a fine needle valve positioned centrally between the two LiF windows and the pressure was measured using a 0–1 Torr capacitance manometer (MKS baratron, type 390 HA) attached by a 6 mm diameter, 30 cm long flexible bellows. During the experiment, the gas sample was continuously refreshed by maintaining a very low input flow which was matched by a corresponding out flow to a pump. In this manner, the sample was replenished whilst minimizing pressure gradients.

To ensure mechanical stability the baratron is designed to operate at an elevated temperature of 45 °C. Thus, thermal transpiration effects [17] between the absorption cell and the sensor assembly need to be taken into consideration to be certain that the correct pressure is being recorded. The effects of thermal transpiration have been investigated by Poulter et al. [18] over an extended pressure range for a variety of gases. To correct the measured pressure reading for thermal transpiration is not straightforward as the calibration factor varies significantly in the pressure range of interest. An alternative method, which was adopted in the present experiment, is to enclose the entire apparatus in a thermally insulated box and to provide thermostatically controlled heating in the box. The temperature in the box was maintained slightly below 45° to enable the baratron to regulate properly. This procedure ensured that no correction was required.

The absolute photoabsorption cross section was obtained through application of the Beer-Lambert law [19]

$$I_t = I_0 \exp(n\sigma l)$$

where I_t is the intensity of the transmitted radiation after passing through the gas column, I_0 is the corresponding incident intensity, n is the gas number density, σ is the photoabsorption cross section and l is the length of the gas column. To determine σ as a function of photon energy, the monochromator was stepped over the chosen