Helium I Photoelectron Spectrum of Disulphur Dinitride

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Summary The photoelectron spectrum of disulphur dinitride has been determined and tentatively assigned.

Interest in sulphur–nitrogen chemistry has been stimulated by the unusual properties of polymeric sulphur nitride

$(SN)_x$, in particular its metallic[1] and superconductive[2] behaviour. The starting point for the synthesis of $(SN)_x$ is the thermal decomposition of S_4N_4 over silver wool, and the subsequent polymerisation of the resulting S_2N_2.[3,4] The mechanism of the polymerisation of S_2N_2 is a matter of particular interest,[5–7] to which a knowledge of its energy levels is relevant. We have obtained identical photoelectron (p.e.) spectra (Figure) from S_2N_2 generated directly into the spectrometer and from a sample prepared in a separate experiment. The spectra of the possible contaminants S_4N_4 and S_4N_2 were also recorded,[8] but no bands from them [or from the high polymer $(SN)_x$][8] appeared in the spectrum of S_2N_2. We note that this species is thermally stable up to 360 °C in the gas phase at low pressure.

The assignment of the p.e. spectrum is not straightforward, since several states are close in energy, and the resolved vibrational structure is complex. The molecule is square,[4] and CNDO,[9] X_α-SW,[6] and *ab initio* investigations[10] agree with simple M.O. arguments in placing 8 M.O.'s in the He I energy range (21·2 eV). The X_α-SW and *ab initio* results agree with the ordering $^2B_{3g}$, $^2B_{2g}$, $^2B_{3u}$, and $^2B_{2u}$ (to low energy) of the first four levels, though the former method groups them more definitely into sets of three and one. We observe only four main bands and, from the relative intensities, we place three vertical ionisation potentials (I.P.) in the first band, which shows discernible vertical I.P.'s at 10·52, 10·86, and 11·05 eV. The adiabatic I.P. is at 10·41 eV, with resolved structure of 470 and 810 cm^{-1}. In view of the relatively sharp Franck-Condon envelope this band is ascribed to a π-ionisation, involving an antibonding combination of S $3p$-orbitals, specifically $^2B_{3g}$, in agreement with the calculations. The second and third I.P.'s are assigned, respectively, to the corresponding non-bonding combination of N π-orbitals ($^2B_{2g}$) and to the in-plane antibonding σ-M.O. ($^2B_{3u}$), the last assignment being made on the basis of a broader Franck–Condon envelope. The well separated band at 12·3 eV (vertical) has complex vibrational structure of 450 and 790 cm^{-1}, corresponding closely to the frequencies of the B_{2u}, B_{3u} S–N stretching modes in the neutral species (476 and 785 cm^{-1});[11] the exact position of the vibrational origin is not clear. We assign the symmetry $^2B_{2u}$ to the band, following the calculated ordering. We would normally expect a broader band from the ionisation of such a σ-bonding level, but in the present case it is more than likely that the constraints of the four-membered ring tend to retain the geometry of the neutral molecule on ionisation.

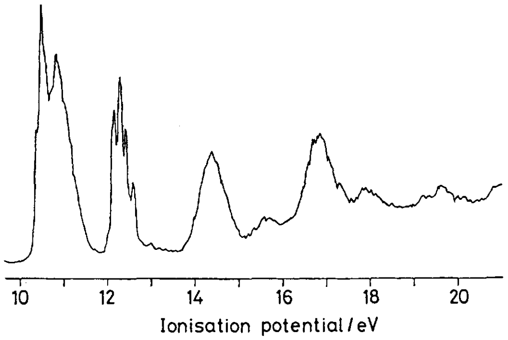

FIGURE. He I photoelectron spectrum of S_2N_2.

The remaining two bands at 14·40 and 16·77 eV are featureless, but following the X_α ordering (which alone groups the levels into pairs) the first contains the $^2B_{1u}$ and ^2A_g states, and the second the ^2A_g and $^2B_{1g}$ states. The spectrum also shows weak structure around 15·5 eV and in the range 17·5—20 eV, which might conceivably arise from previously unrecognised sulphur nitrides, but it is not impossible that the bands arise from additional ionisations.

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