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DOUBLE EXCITATION IN THE K - SHELL ABSORPTION SPECTRUM OF SULPHUR IN H_2S AND D_2S

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Abstract

The X- ray absorption spectra of H_2S and D_2S were studied near the sulphur K - edge at high resolution using synchrotron radiation as a continuous background source. In addition to the well-known single electron excitation lines we observe two new structures in the continuum. On the basis of single configuration Hartree - Fock calculations we assign these features to two-electron transitions leading to levels of the final state configurations $1s2s^2p^63s^2p^34s$ np,ns, 4p np and 3d np and to excited states of the ion $1s2s^2p^63s^2p^3$ ns, np, nd εp.

1. Introduction

Progress in the understanding of the x-ray absorption near edge structure within about 50 eV from threshold - now named XANES or NEXAFS - was much slower than that of the extended structure - now called EXAFS - because of the complex physical phenomena occuring near the ionisation threshold. In molecular spectra for example, Rydberg and valence states, shape resonances due to multiple scattering and "shake" peaks have been postulated to be of importance /1/. The latter multi electron transitions, involving the simultaneous change of states of two or even more electrons, are hardly observable in molecular spectra because of the much stronger structure of molecular origin. Such transitions were already predicted by Heisenberg in 1925 /2/ but were detected not before the mid - sixties in the absorption /3/, the shake-up photoelectron spectra of rare gases /4/ and only recently in the X - ray absorption spectra of solids /5/. Multi-electron effects are still an object of theoretical studies of ground and final state correlation phenomena /6/ as they support and check these theories.

The purpose of the present letter is to report our new measurements of the K photoabsorption spectrum of sulphur in gaseous H_2S and D_2S where emphasis is put on the structure above the first ionisation limit which was partly observed by Bodeur and Esteva /7/ in their recent synchrotron radiation absorption experiment. Because of much higher intensity we were able to measure the structure more clearly, to observe more structure at higher energies and to resolve even some fine

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structure in the broad low energy feature. Based on a series of single configuration Hartree-Fock calculations the observed structures are assigned to atomic transitions showing the existance of double excitation also in molecular spectra.

2. Experimental

Our measurements were carried out between 2450 eV and 2550 eV at the Bonn 2.5 GeV synchrotron running at 2.0 GeV with an electron current of about 30 mA. The spectra were obtained by standard X-ray absorption techniques. The monochromatized radiation is monitored by an ionisation chamber before passing through the sample cell. A second ionisation chamber is used as the detector.

A double crystal monochromator similar to the one described by Lemonier et al. /8/ was used and equipped with Si (1,1,1) crystals, whereby the second order radiation is effectively suppressed so that higher orders contribute less than 0.5 per cent of the signal. From comparison of the K - shell absorption of atomic Ar with published data in the literature /9/ and from the rocking curve of our crystals the instrumental resolution was estimated to be about 0.5 eV in the energy range of interest. The energies of the reported spectra were calibrated in simultaneous runs against the known Ar K-edge /9/. The accuracy of our energy positions is estimated to be better than $\pm$0.4 eV. Both ionisation chambers were filled with air to about 100 Torr . The sample cell had a length of about 12 cm and was separated from the ionisation chambers by vacuum tight 16 mm diameter windows consisting of a 12 um thick capton film. The pressure in the cell was controlled by a calibrated pressure sensor (Datametrics) and was varied between 1 Torr and 20 Torr for the measurements reported here. The preamplified currents from the ionisation chambers were digitized and were read out by a Commodore CBM 3032 micro computer at least 10 times before the monochromator was set by the computer to the next wavelength. Step size was varied between 0.02 and 0.04 eV for different runs.

3. Results and Discussion

The K-shell absorption of H_2S recorded at a pressure of about 10 Torr is shown in figure 1. Displayed are original data without any processing. Up to the first ionisation limit this spectrum agrees very well with those reported previously by several other authors. The energies of the lines labelled 1 to 3 in this figure (2472.4 eV, 2475.5 eV and 2476.8 eV) agree very well with those given by LaVilla /10/ and Mazalov et al. /11/. Included in this figure are positions of single electron excitations 1s $\rightarrow$ np ($n \geq 3$) calculated using a Hartree - Fock program /12/. The calculated energy positions were adjusted relative to the measured ionisation potential of 2478.5 eV /13/. A comparison of the measured and calculated lines strongly supports the assignment of these lines as given by Lavilla /10/ and and Mazalov et al. /14/ which was confirmed also by Bodeur and Esteva /7/ on the basis of unpublished results of Langhoff. The first line is molecular

in origin and is assigned to a transition to the antibonding orbitals $3b_2$ and $6a_1$ Lines No 2 (2475.4 eV) and No 3 (2476.8 eV) may with good confidence be assigned to the second and third member of the 1s $2s^2 3^2 3p^4 np$ (n≥3) Rydberg series.

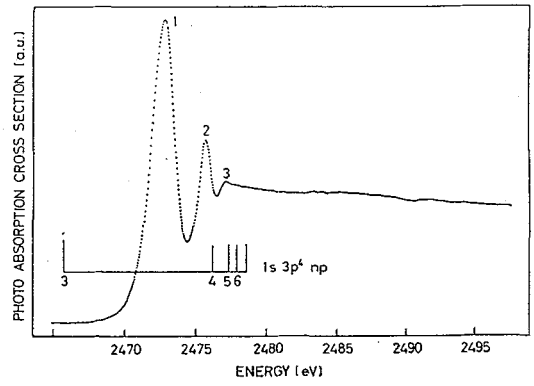

Fig.1: Sulphur K-shell photoabsorption cross section in H_2S

Above the first ionisation potential we observe some fine structure with small amplitude which is barely visible in figure 1. This structure turned out to be reproducible regarding shape and position under different experimental conditions and was also observed in our D_2S spectra. In figure 2 we show on an enlarged scale the part of the H_2S spectrum extending beyond peak No 3. To make the fine structure observed in this region stand out more clearly a smooth background was subtracted from the spectrum in figure 1 where the form of the background did not change either the shape or the position of the reported bands. We observe a broad feature (4-6) between about 2482 eV and 2490eV with some fine structure at the low energy side and a second less broad line (7) centered at about 2491.7 eV. As suspected by Bodeur and Esteva who observed the first part of the low energy structure these structures could be either shape resonances or double excitations.

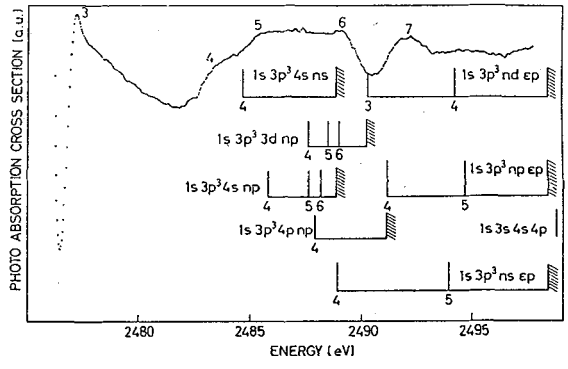

Fig.2: Sulphur K-shell photoabsorption in the double excitation region

An assignment to a molecular shape resonance seems to be unlikely as hydrogen is a very weak backscatterer. Therefore we believe all structure to be due to atomic

double excitations. To confirm this assignment we have performed a series of single configuration Hartree-Fock calculations the results of which are also included in figure 2. As the excited core ionisation limits of H_2S are not known all line positions in figure 2 are not adjusted but given as calculated.
In our calculations we have included the lowest possible shake-up transitions as well as some conjugated shake-up series. As the sticking diagrams in figure 2 show, all transitions into doubly excited states of the atom including the excitation of a 3p electron severely overlap in the region of the broad structure (5-6). Feature No 7 is probably due to the lowest transitions to excited states of the ion though the correspondence is not as clear as for the structure (4 - 6). One has to keep in mind though, that the energies given in the sticking diagram are not adjusted and carry an uncertainty of several eV as estimated from the difference between experiment and our calculation of the first ionisation limit. In view of this uncertainty the assigned transitions quite satisfactorily fit the observed features. It even appears possible that the transition due to the doubly excited state $1s2s^2 3s3p^4 4s4p$ contributes to the second structure. A more specific assignment is not warranted since severe overlap is expected in view of the calculated line density and the natural widths of the lines which in most cases exceed the line spacing within a Rydberg series. The situation is even worse than indicated as our sticking diagrams give only the centers of gravity of the configurations, whereas most of the configurations, having up to four open shells, consist of numerous levels spread sometimes over several eV and more. Thus the applicability of the single configuration calculations used here is at least questionable. We believe this to be an example where the method of unresolved transition arrays (UTA's) developped by Bauche-Arnoult et al. /15/ for transitions of highly ionized ions could be favourably applied.

4. Conclusion

In the region above the first ionisation potential we have observed a weak but reproducible fine structure in the spectra of H_2S and D_2S. The double excitation Rydberg series which we have calculated with a non relativistic Hartree-Fock program coincide favourably with these features. From this finding we feel compelled to assign all observed structure to doubly excited states. Since the values for the excited core ionisation limits are unknown and various series severely overlap each other a more detailed assignment is not appropriate.

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