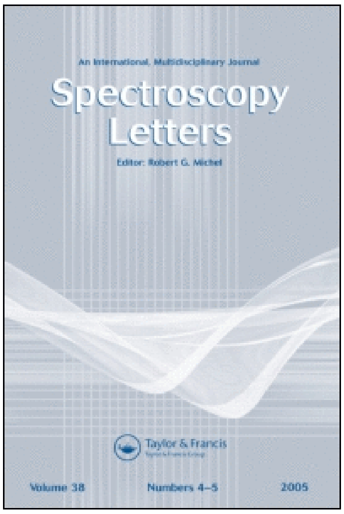

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Vacuum Ultraviolet Spectrum of the SO Radical

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VACUUM ULTRAVIOLET SPECTRUM OF THE SO RADICAL

Key Words: Vacuum Ultraviolet; SO radical.

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ABSTRACT - Previous work on the vacuum ultraviolet spectrum of the SO radical is reinterpreted and several new transitions reported.

The photoelectron spectrum (P.E.S.) of the SO radical has recently been reported[1] and the first ionisation potential (adiabatic) given as 10.34 eV. Previous work on the vacuum ultraviolet spectrum of this radical[2] had indicated an approximate ionisation potential in reasonable agreement with this and had allowed a reinterpretation of two earlier results, all of which now agree within experimental error.[1,2] However, the assignment of the shortest wavelength transition in the SO spectrum[2] now requires revision, in view of the more precise photoelectron data. We here discuss the reassignment and report some new transitions.

The SO radical was produced by flash photolysis of SO_2 in the presence of a large excess of diluent gas ($P_{SO_2} = 13.3\ Nm^{-2}$; $P_{He} = 53.2\ kNm^{-2}$). The experimental arrangement used, has been described previously.[2] Only a small fraction of the SO_2 was photolysed, however, the spectrum of this molecule is limited to relatively narrow regions for wavelengths greater than 130 nm, and transient spectra could be observed without undue interference by the parent molecule. In addition to the spectrum of the SO radical, numerous transitions arising from atomic sulphur (S^3P_J) were observed and presumably result from secondary photolysis of the SO radical. Transitions arising from atomic oxygen would be obscured by emission lines from our continuum source and were thus not observed.

The SO($D \leftarrow X$) transition has been described previously[2] and attributed to the promotion of a π^*3p electron to a 4s Rydberg state associated with the sulphur atom. Using the value obtained for the ionisation potential from P.E.S.[1] a value for the quantum defect of δ =2.06 is found, which is close to that observed for the same series in atomic sulphur, and thus confirms the previous assignment.[2] The second transition at approximately 147 nm ($E \leftarrow X$) is very similar in appearance to the ($D \leftarrow X$) transition and was attributed[2] to the second member of the ns Rydberg series. However, it is now clear from the P.E.S. data that this transition is more reasonably assigned as the first member of the nd Rydberg series with $\delta = 0.3$ (the corresponding defect in atomic sulphur is $\delta = 0.3$). The electronic configurations --- $\pi^*3p(4s)$ and --- $\pi^*3p(3d)$ both give rise to $^3\Pi$ electronic states, to which transitions from the ground state ($X\ ^3\Sigma^-$) would be fully allowed. The similarity in appearance between the $D \leftarrow X$ and $E \leftarrow X$ transitions may thus be accounted for, and the previous discussion of spin orbit coupling retained to interpret the observed structure.

The new transitions reported here are collected in table 1, together with the calculated values for the quantum defects.

TABLE 1

New Transitions of SO

λ (vacuum)$^{nm.}$	ν m^{-1} (X 10^2)	δ
142.04*	70,403	2.09
141.37	70,736	2.06
140.68	71,083	2.02
138.86	72,015	1.90

*error in wavelength measurements, ±0.05nm.

The three bands between 140-142 nm are most reasonably assigned to the spin-orbit components arising from the second member of the ns Rydberg series (n = 5). The intensity of the transition is significantly less than that of the first member; however such effects are commonly encountered in Rydberg series. It was not possible with the resolution available to determine whether the bands exhibit discrete rotational structure. The spin-orbit splitting is clearly greater than that observed in the D←X system and indicates a tendency towards (Ω_c,ω) coupling, similar to that observed for S_2 in this region.[3] The weak band at 138.86 nm may be associated with the (1,0) transition of the same system.

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