

Short Communication

Two-photon dissociation of SO₂ in the region 285 - 311 nm

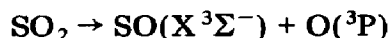
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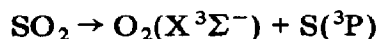
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It is shown by two-photon laser-induced fluorescence that a two-photon absorption by SO₂ in the wavelength region 285 - 311 nm produces as primary products S(³P) and S(¹D) atoms as well as SO molecules.

The threshold energies for the dissociations



and



are 5.65 eV (219 nm) and 5.90 eV (210 nm) respectively. However, intense sources of light at energies less than the threshold energies have been shown to dissociate SO₂. One technique used light at 248 nm so intense that not only did fragmentation occur but the photofragments were also excited [1, 2]. Specifically SO was excited to a B state by a one-photon absorption and S(³P) was excited by a two-photon absorption to a high-lying state which decayed to the 4³S state. Emission from the B and 4³S states was observed. In this communication a similar one-laser experiment is described in which the same wavelength was used to dissociate the SO₂ molecule (probably by a two-photon absorption) and to excite fluorescence from the fragments by a further two-photon absorption.

The experimental technique has been described before [3, 4]. Briefly the polarized light of a YAG-pumped dye laser (pulse width, 10 ns; bandwidth, 0.12 cm⁻¹; repetition rate, 5 Hz) frequency doubled with a potassium dihydrogen phosphate crystal is focused into a cell through which SO₂ at 100 mTorr flowed. A solar blind photomultiplier tube is mounted on top of the cell. The signal seen after each laser pulse is sent to a preamplifier and then to a boxcar integrator. The output of the latter was fed to a strip chart recorder.

It has recently been shown [3] that sulfur atoms in their ground 3³P_{J'} ((3p)⁴) states are excited by two-photon absorptions to the 4³P_{J'} ((3p)³(4p)) states. The range of the various J' ← J'' transitions is 3.99 - 4.02 eV (311 - 308 nm). The excited 4³P_{J'} radiates in the IR, decaying to the 4³S⁰ state

and then returns to the ground state by emitting a 180.7 nm photon. Similarly sulfur atoms in the 3^1D_2 state absorb two photons with energy of 4.30 eV (288.2 nm) and are excited to the 4^1F_3 ($(3p)^3(4p)$) state. Atoms in this state radiate to an intermediate 4^1D_2 state and thence decay to the ground state with emission of a 166.7 nm photon.

Vacuum UV emission was detected when light with the above-mentioned wavelengths was focused in SO_2 gas. The excitation spectrum consisted of sharp lines exactly at the known positions for sulfur atoms, showing that the atoms were undergoing a two-photon absorption (in contrast with a four-photon absorption by the molecule). This is a simultaneous two-photon absorption to be distinguished from the probably sequential two-photon absorption of SO_2 . In the 285 - 311 nm region considered here SO_2 has a weak absorption and a long radiative lifetime. Hence there is an opportunity for a second photon to be absorbed within the 10 ns duration of the dye laser pulse. Incidentally, from the intensities observed it could be inferred that the population of the different J'' states was statistical, *i.e.* proportional to $2J'' + 1$.

In addition to sulfur atoms the SO molecule was also detected. By absorbing two UV photons SO is excited from its ground $X^3\Sigma^-$ state to the Rydberg $E^3\Pi$ state which decays to the ground state by vacuum UV emission. The (0,0) and (1,0) band heads were seen at 147.6 nm and 145.0 nm respectively. The $E \leftarrow X$ transition has been seen in absorption at low resolution [5] but the spectrum has not been completely analyzed. Consequently we did not attempt to extract a rotational distribution from our spectrum.

In this work we have shown that when the energy of two photons (equivalent in energy to a single 142.5 - 155.5 photon) is deposited in an SO_2 molecule, dissociation takes place into $S(^3P, ^1D)$ atoms and O_2 molecules as well as SO molecules and oxygen atoms. It had previously been shown that at 193 nm [6, 7] dissociation is only to SO and O but at 147.0 nm and at 123.6 nm to an even greater extent dissociation to $S + O_2$ is also found [8]. Left unanswered are two questions. First does the sequential absorption of two photons each of energy $\hbar\omega$ reach the same region of configuration space as the absorption of a single photon of energy $\hbar(2\omega)$? Secondly does a single excited surface lead to both types of exit channels or can the excited surfaces be categorized as leading to one or the other set of reaction products?

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