Preliminary Note

The direct observation of Te(5¹D₂)

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Despite considerable effort in a number of laboratories, the only direct study of the kinetics of a Group VI atom in the ns^2np^4 $^1D_2$ electronic state is that for $O(2^1D_2)$, which has been observed *via* the forbidden emission[1]:

$$O(2^1D_2) \rightarrow O(2^3P_J) + h\nu(630 \text{ nm}).$$

Thus only in the case of oxygen can the large body of relative rate data, which now exist, be placed on a reliable absolute basis; and even for oxygen controversies still exist, particularly concerning the data for quenching of $O(2^1D_2)$ by CO_2[2].

Osborne[3] has previously reported the observation of $Te(5^1D_2)$, in absorption *via* the 277.1 nm transition, during a study of the combustion of H_2Te, but did not study its kinetics. Thus none of the Group VI atoms have hitherto been studied kinetically in absorption, although this method is undoubtedly several orders of magnitude more sensitive than monitoring the forbidden emission. The main problem in detecting atoms in the $^1D_2$ state arises from their high reactivity and thus rapid removal from most convenient systems; both quenching and chemical reaction proceed in most cases at rates approaching the gas kinetic collision frequency.

We here report the direct observation of $Te(5^1D_2)$ following the flash photolysis of D_2Te. The apparatus has been described previously[4], and consisted of a conventional flash photolysis unit coupled with a vacuum spectrograph, and ancillary equipment to permit time resolved observations in the wavelength region 250–130 nm. The flash lamp and reaction vessel were constructed of Vitreosil quality quartz, thus restricting photolysis to $\lambda \geq 200$ nm. Spectra were recorded on Ilford HP4 film sensitized for low wavelengths by immersion in 0.5 M sodium salicylate solution in methanol[4]. The D_2Te was prepared by the action of D_2O on aluminium telluride, using a conventional high vacuum line, and purified by trap to trap distillation; traces of the impurities CS_2 and H_2S were removed by pumping on the sample at 193K. Despite attempts to remove all traces of H_2O from our system (by exposing it repeatedly to samples of D_2O, and passing a Tesla discharge through the gaseous D_2O) the final sample of D_2Te was still found to contain small traces of HDTe and H_2Te.

We have examined the photolysis of both H_2Te and D_2Te, however, in the former case, a strong band due to H_2Te obscures the strongest absorption line of $Te(5^1D_2)$ and prevents quantitative measurement of its kinetics. We have therefore used D_2Te, for which the appropriate region is not obscured by the molecular spectrum[5].

The excited atom was observed *via* the $(7^5D_J{}^\circ \leftarrow 5^1D_2)$ transition at 175.8 nm[6]. Other weaker transitions to longer wavelengths were also observed, but were too weak for kinetic studies. The most probable mechanism for the formation of $Te(5^1D_2)$ is direct elimination in the primary photochemical step:

$$D_2Te \xrightarrow{h\nu} D_2 + Te(5^1D_2) \tag{1}$$
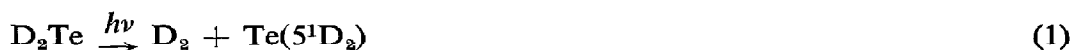
as it is observed most strongly at very short delays ($10\mu s$); some photolysis yielding DTe also occurs as this radical is observed weakly at short delays. This latter process is known to be the major primary step in the ultra-violet photolysis of H_2O; however, a consideration of the molecular orbitals expected at higher energy (lying at energies corresponding to the vacuum ultra-violet region) indicates that direct elimination may occur at short wavelengths[7]. The absorption spectrum of D_2Te is considerably shifted, to longer wavelengths[7], compared to that of water and it is thus reasonable that reaction (1) occurs in the ultra-violet photolysis of D_2Te.

The decay of $Te(5^1D_2)$ is illustrated in Fig. 1. It can be seen that the decay is relatively slow, and under appropriate conditions we have been able to observe
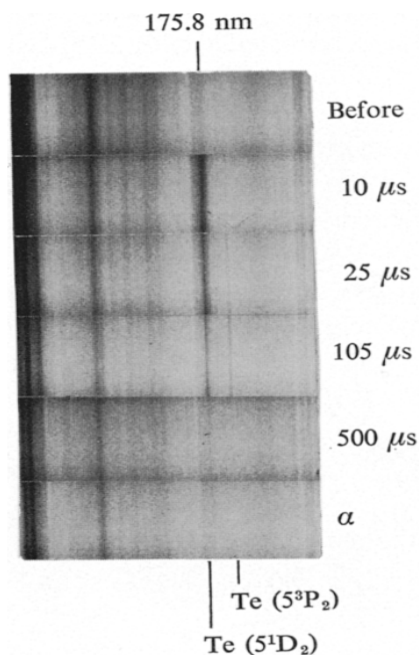

Fig. 1. Decay of $Te(5^1D_2)$; $P_{D_2Te} = 4.0$ N m^{-2}; $P_{He} = 50$ kN m^{-2}; $E = 800$ J.

this excited state for periods up to 500 μs. Careful analysis of the decay kinetics reveals that during the first 60 μs a rapid decay occurs, followed by a slower rate of decay at longer times (60–500 μs). We believe that the rapid initial decay is due to radical–radical reactions, even at the relatively low concentrations present in our system ($\sim$2 N m^{-2}). However, we have been unable to determine with certainty the species responsible; possibilities are: hydrogen atoms, or tellurium atoms in the $^3P_1$ or $^3P_0$ states. Other radicals such as HTe, Te(5^3P_2) or Te$_2$, are present at times when the slow decay is observed and thus cannot be responsible for the rapid initial relaxation. The decay for times greater than 60 μs, shows reasonable first order kinetic behaviour, being independent of the pressure of helium, but first order with respect to the concentration of D$_2$Te. The decay of Te(5^1D_2) is accompanied by a growth in the concentration of DTe, and we attribute this to the reaction:

$$Te(5^1D_2) + D_2Te \rightarrow 2DTe \tag{2}$$

In addition to this reaction, the atomic resonance transition at 214.4 nm ($6^3S_1{}^\circ \leftarrow 5^3P_2$) is observed to grow as Te(5^1D_2) decays, and it is concluded that some relaxation occurs parallel to reaction (2). Another atomic line at 175.1 nm shows similar kinetic behaviour to the 214.4 nm line and is most probably associated with a transition from Te(5^3P_2) to the 7s orbital (the vacuum ultra-violet spectrum of atomic tellurium has received relatively little attention and a number of transitions do not appear to have been observed or analyzed). The absolute rate for the removal of Te(5^1D_2) was found to be (1.0 $\pm$ 0.2) $\times$ 10^{-11} cm^3 molecule^{-1} sec^{-1} which is about a factor of three slower than the rate reported for O(2^1D_2) with H$_2$O[8].

The effect of quenching by the noble gas, argon, was also examined. For O(2^1D_2) and S(3^1D_2), quenching by argon occurs at approximately one in 100 collisions[9]. However, for Te(5^1D_2) we have been unable to detect any quenching by argon for pressures up to 13.3 kN m^{-2} which corresponds to a collision efficiency of less than 10^{-5}.

We intend to extend these observations, and to examine quenching by the other noble gases, and the reactions with molecules including H$_2$ and D$_2$.

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