Laser Photolysis of CD_3I in the Ultraviolet: Formation of Highly Excited Iodine Atoms

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Summary Highly excited and potentially reactive iodine atoms, $I(5p^46s^2P_{3/2})$ are produced by u.v. multiphoton excitation of CD_3I with a rare-gas halogen exciplex laser.

MULTIPHOTON excitation using high power u.v. lasers provides a means of producing highly excited electronic states of atoms and free radicals.[1,2] The chemistry of such states is as yet little understood[3] and offers a new frontier to the chemist.

We here report the observation of highly excited iodine atoms, I($5p^46s^2P_{3/2}$) following photolysis of CD_3I (weaker signals were also observed with CH_3I) at 193 nm with a rare-gas halogen exciplex laser (Lambda Physik EMG 500). Unfocused laser pulse energies of 2—10 mJ (14 ns duration, *ca.* 1 MW peak power) were employed and fluorescence was observed at right angles using a monochromator and photomultiplier, following the passage of the laser beam through a simple cross-shaped fluorescence cell. The latter was connected to a conventional high-vacuum line and samples of CD_3I were outgassed and fractionally distilled before admission to the fluorescence cell. Samples were subjected to a single laser pulse as even stronger fluorescence, in several regions of the u.v., was observed from the photolysis products (preliminary studies indicate these to be I_2 and CD_2I_2: we are currently investigating the photolysis of these molecules).

Fluorescence was observed at 206·2 and 178·3 nm from the single upper level, I($5p^46s^2P_{3/2}$), which lies 56,093 cm^{-1} above the ground state. The intensity of these lines was found to increase quadratically with laser power, indicating that at least two photons are required for the excitation process (this is also expected on energetic grounds).

John *et al.*[4] have shown that the close-lying I($5p^46s^4P_{5/2}$) atom reacts rapidly with CH_4 by abstracting a hydrogen atom, but this appears to be the only study of highly excited iodine atoms. If abstraction proceeds adiabatically, as expected, this should lead to the formation of electronically excited HI molecules, which should be detectable in fluorescence. Further work on this, and other highly excited states of the iodine atom is desirable and the present work indicates a new approach to the area.

We have also detected fluorescence from the $A^2\Delta$ and $B^2\Sigma^-$ states of the CH radical[5] following laser photolysis of CH_3I at 193 nm and plan to explore the mechanism for formation and the chemistry of these excited states in the near future.

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