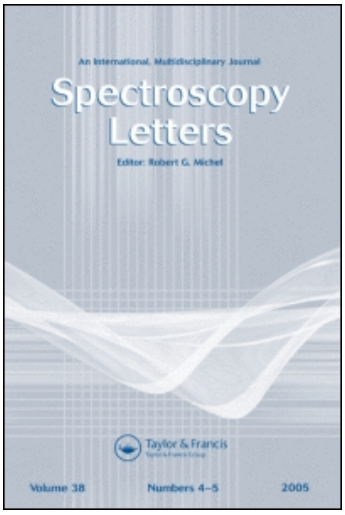

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Excited Atoms in the Flash Photolysis of some Germanium Compounds

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We have recently reported measurements of the rates of the collisional relaxation of various atoms amongst the spin-orbit components of their ground electronic states; an approximate correlation exists with other types of molecular energy transfer.[1-3] We present here an outline of some qualitative observations of the production and relaxation of $Ge(4^1D_2)$ and $Ge(4^3P_J)$ in the flash photolysis of a number of germanium compounds. Atomic germanium was selected for study because the ground state comprises a 'normal' Landé multiplet and should exhibit 'inverted' relaxation as compared for example to $Fe(a^5D_J)$ which equilibrates initially in the high energy substates. The low lying states of germanium are listed in table 1.[4] The flash photolysis apparatus was of standard design[1-3] and spectra were recorded with a Hilger medium quartz spectrograph.

Table 1

State	4^3P_0	4^3P_1	4^3P_2	4^1D_2	4^1S_0
Energy (cm^{-1})	0	557	1410	7125	16367

Excited atomic germanium was detected in absorption in the flash photolysis of $Ge(C_2H_5)$, $GeCl_4$ and $GeBr_4$. Some of the observed transitions are shown in fig. 1. A comparison of the intensities at the three time

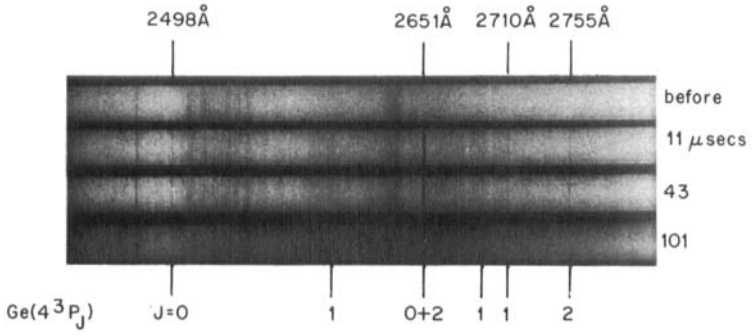

FIG. 1

delays showed that the initial population in the ground substates is non-Boltzmann because the ratios $Ge(4^3P_{1,2})/Ge(4^3P_0)$ decrease with time. The large excess of argon prevented the occurrence of any significant change in the temperature of the environment. Atoms were also detected in the (4^1D_2) state from the transitions at 2198 Å and 2418 Å. Excited atoms are produced by the secondary photolysis of germanium monohalide intermediates. These preliminary experiments illustrate the possibility of measuring the absolute rates of the energy transfer processes and the chemical reaction rates of the free atoms.

A number of new molecular band systems were detected inadvertently in this research and the wavelengths of the bands have been recorded.[5] Since no rotational analysis could be attempted the results are mentioned here in brief outline. In the flash photolysis of $Ge(C_2H_5)_4$ a curiously sharp and intense feature was detected in absorption at 2465 Å, together with a weak band at 2483 Å. In flashed $GeCl_4$ the GeCl system at ~ 2800 Å of Jevons, et al.[6] was recorded in absorption and the positions of a number of new bands were entirely consistent with their vibrational analysis. Several new systems probably all due to GeCl, were observed at shorter wavelengths down to 2150 Å. In flashed $GeBr_4$ the GeBr system of Jovons, et al.[6] (~ 3000 Å) was recorded and their vibrational assignment was confirmed

and extended. Several new systems apparently of GeBr and possibly $GeBr_2$ were observed in the 2100-2500 Å region. The new germanium halide spectra were discovered simultaneously and independently by Oldershaw and Robinson.[7] Gaseous GeO could be produced in all these systems by addition of oxygen. No detailed study of any of these spectra will be attempted.

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