would be designed to produce and take advantage of the predicted increased charged particle density.

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Vacuum Ultra-Violet Absorption Spectra of Flash-heated Lead reacting with Various Gases

RECENT investigations of the hot atom chemistry of lead-212 recoiling from α-decay of polonium-216 have shown that energetic lead atoms can react with gases such as methane to form volatile compounds[1]. In the recoil reactions, the lead species originate with high kinetic energy and are afterwards degraded by collisions, eventually reacting to form stable compounds.

In an effort to determine whether gaseous lead atoms could react at essentially thermal energies (< 1 eV.) to give products similar to those observed in the recoil studies, the present investigations were undertaken.

The techniques of flash heating lend themselves ideally to the study of thermalized metal atoms in the gas phase because of the ability to vaporize fairly significant quantities of material in the presence of a surrounding medium that is only slightly heated[2]. Combination of flash heating with kinetic absorption spectroscopy allows the detection and examination of short-lived species in the vapour-phase during the reaction[3].

Using the techniques previously described[3], about 8 or 10 mgm. of lead was vaporized per flash. The metallic lead in the form of a thin ribbon (0·0005 in. thick, 1/8 in. wide) was wound on a quartz support so as to pass through the optical path within the cell and replaced the carbon grids used in the earlier work.

The usual spectral region photographed extended from 1300 to 3300 Å. This region includes the Rydberg series leading to the ionization limit of PbI at 1671·65 Å., corresponding to transitions from the ground-state ($6p^2\ {}^3P_0$) (ref. 4).

All spectra taken within a few milliseconds after the beginning of the preparative photoflash showed absorption lines due to lead atoms in the ground-state. Transitions from the first and second excited states were also observed. These lie 7,819·35 and 10,650·47 cm.$^{-1}$, respectively, above the ground-state and correspond to the configurations $6p^2\ {}^3P_1$ and $6p^2\ {}^3P_2$ (ref. 4). No evidence for ionization of the vaporized lead was obtained.

Reactions of lead vaporized in the presence of CF_4 or SF_6 resulted entirely in fluorine abstraction from the parent fluorinated molecule by the metal atoms, yielding lead monofluoride. The monofluoride was identified from the band systems near 2100, 2500 and 2800 Å.[5,6]. The PbF could be observed from the time of maximum light intensity until about 700μ later. After this period, light scattered by particles formed by further reaction of PbF caused a heavy continuous absorption and prevented subsequent spectral observations. Many new vibrational bands and an apparently new system in the 1800–1900 Å. region have been observed in association with PbF in these studies. Rotational fine structure was clearly observed, particularly in the 2800 Å. region.

Table 1. SPECIES OBSERVED BY FLASH HEATING AND KINETIC SPECTROSCOPY OF LEAD IN VARIOUS GASES

Short-lived atom or molecule	Gaseous matrix	*Delay times (μs.)	Wave-lengths (Å.)
Pb ($6p^2\ {}^3P_{0,1,2}$)	All	0–1300	1600–3300
Pb	,,	,,	bands at 2136, 2143, 2161, 2167
PbF	SF_6 CF_4	0–1050	band systems at 1900, 2100, 2500, 2800
PbO	CD_4+air O_2	45–1000	band systems from 2800 to 3700
Unidentified	C_2H_6 CH_4 D_2 (2900 Å. only)	180–420	band systems at 2400, 2900
CO (excited)	CO	1000	1700
O_2 (excited)	O_2	180	2000–2500
Emission lines	vacuum SF_6 CF_4 Ar CO	0–1000	1587, 1634, 1661

*Delay times refer to time elapsed between peak intensity of preparative flash and peak intensity of spectroscopic flash.

PbO was produced by reactions of flash-heated lead with oxygen or with air present as an impurity in methane. Band systems for PbO lie mostly in the wave-length regions above 2800 Å. (ref. 5).

In the presence of methane or ethane, unidentified diffuse transient systems were observed in the regions near 2400 and 2900 Å. The system at 2900 Å. was faintly visible when the flash heating was carried out in a deuterium atmosphere, indicating a possible hydride formation.

Since it was desired to limit these studies as much as possible to thermally initiated reactions, gases were chosen so as to be transparent to the light used and to minimize photochemical processes. Table 1 summarizes the gases used and the absorptions observed at various delay times following peak intensity of the preparative flash.

Of special interest are the diffuse bands observed at 2136, 2143, 2161 and 2167 Å. These occurred in all the gases and in vacuum and have tentatively been assigned to the $Pb_{2(g)}$ molecule.

The absorption spectra were supported by mass spectrographic analyses in showing that no volatile compounds analogous to those reported for the recoil lead-212 studies[1] were produced by reactions in methane, methane and air, carbon monoxide or argon.

Complete analyses of the spectra are in progress in an effort to determine electronic temperatures of the vaporized lead atoms and vibrational and rotational temperatures of the product molecules. Additional efforts are being made to identify the emission lines (Table 1) and the unidentified systems near 2400 and 2900 Å.

This work was done in the Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

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