New Metastable State of Mercury*

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A state of Hg with an excitation potential of 9 v has been found to be metastable. It is most likely the $^3D_3$ state of the configuration $(5d)^9(6s)^2(6p)$. It is possible that other members of this configuration also are long-lived. The use of alkali metals as detectors for metastable atoms is discussed.

IT is well known that the lowest $^3P_2$ and $^3P_0$ states of Hg are metastable,[1] since radiation to all lower lying levels (Fig. 1) is forbidden by parity or angular-momentum (J) selection rules. The observations described in this note lead to the conclusion that at least one additional state of Hg is metastable.

EXPERIMENT AND RESULTS

A collimated beam of mercury atoms was bombarded by electrons of controlled energy. The metastable atoms so produced ejected electrons from metallic plates, and the resulting current was measured.[2]

Figure 2 shows Hg excitation functions for two different metal detectors. The curve taken with sodium has a large peak with an appearance potential of 5.4 v, and a smaller peak at higher energy. The curve obtained with platinum shows only the higher energy peak, with an appearance potential of 9.0 v.

An attempt to measure the lifetime of the metastable atoms was made by moving the Pt detector 10 cm farther away from the source. The intensity decreased slightly, by 0 to 10% depending on the electron energy. This indicates that the metastable states involved have lifetimes of the order of 10^{-2} sec or more.

DISCUSSION AND CONCLUSION

The peak of 9 v was quite unexpected. The work function of Pt (5.3 v)[3] is high enough to exclude detection of the known metastable states of Hg. It is necessary to attribute the observations with a Pt detector to a new metastable state with an excitation potential of 9.0 v.

The electron configuration of the ground state of Hg is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}(4s)^2(4p)^6(4d)^{10}(4f)^{14}(5s)^2(5p)^6(5d)^{10}(6s)^2$. The only metastable states[4] arising from excitation of a single s electron are $(6s)(6p)$ $^3P_{2,0}$. Therefore, the 9 v state must belong to the configuration $(5d)^9(6s)^2(6p)$; $^3P_{2,1,0}{}^\circ$, $^1P_1{}^\circ$, $^3D_{3,2,1}{}^\circ$, $^1D_2{}^\circ$, $^3F_{4,3,2}{}^\circ$, $^1F_3{}^\circ$, for all other configurations give states which lie above the ionization potential.

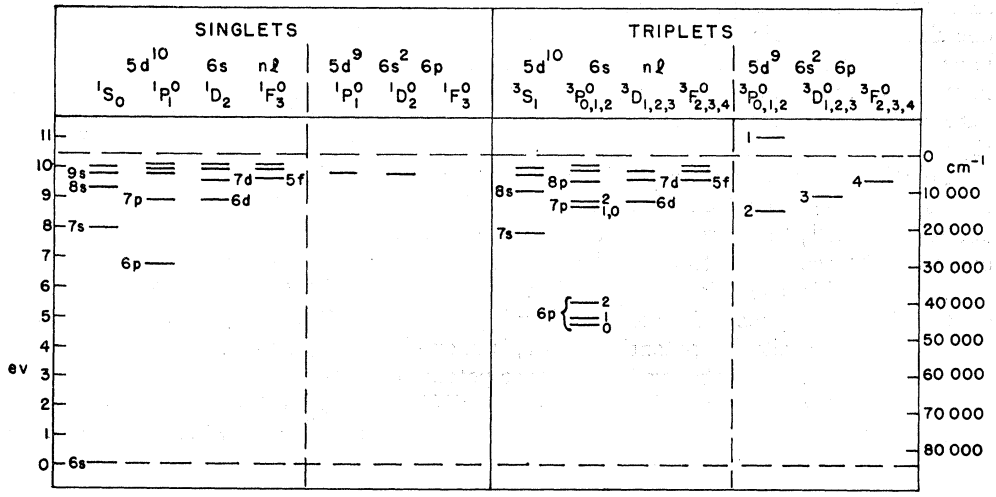

FIG. 1. Energy level diagram for Hg.

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[1] A metastable atom can give up its excitation energy by collision with the walls of the container. For apparatus with dimensions of the order of cm and atoms with velocities of the order of 10^4 cm/sec, metastable atoms have lifetimes of the order of 10^{-4} sec or longer.

[2] For details of apparatus and procedure, see W. Lichten, Ph.D. thesis, University of Chicago, 1956 (unpublished); also J. Chem. Phys. **26**, 306 (1957). By means of an additional device, a retractable LiF window, it was verified that the detector current due to photons was negligible.

[3] All work functions in this note are taken from the compilation of H. B. Michaelson, *Handbook of Chemistry and Physics*, edited by C. D. Hodgman (Chemical Rubber Publishing Company, Cleveland, 1953), thirty-fifth edition.

[4] States with configurations $(6s)(nl)$, where n and l are extremely high quantum numbers, are metastable by the previous definition. However, these lie close to the ionization limit, far from 9 v.

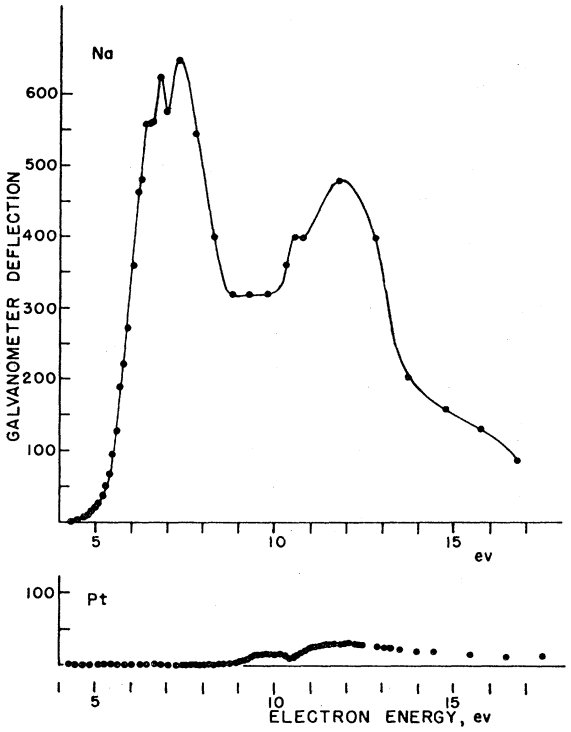

FIG. 2. Excitation functions for Hg, with Na and Pt detectors.

The $^1D_2$, $^3D_2$, and $^3D_3$ states can make transitions only to $(6s)(nd)$ $^1D_2$, ^3D or $(6s)(ns)$ ^3S; all other transitions are forbidden. However, these transitions represent two-electron jumps and are forbidden by the one-electron jump rule. Since the $(5d)^9(6s)^2(6p)$ D states have odd parity, they are free from perturbation by most D states. Thus the configurations are unusually pure, and the one-electron jump rule probably is fairly rigorously obeyed here.

In particular, the $^3D_3$ state can only radiate downward to $(6s)(6d)$ $^3D_{2,3}$. The transition energy here is only about 1700 cm^{-1}; this corresponds to a lifetime of the order of 10^{-4} sec for a strongly allowed one-electron jump. Since this transition is a much weaker two-electron jump a lifetime of 10^{-2} sec certainly is possible. In addition, the excitation potential, 9.05 v, is in excellent agreement with the observed appearance potential of 9.0 v. Thus, it seems very likely that Hg $(5d)^9(6s)^2(6p)$ $^3D_3$ is metastable.

TABLE I. Effective energies of alkali metals for detecting metastables.

Metal	Minimum energy (ev)	Work function (ev)
Li	6.6	2.5
Na	5.3	2.3
K	4.6	2.2
Rb	4.1	2.1
Cs	3.8	1.8

The lifetime measurements seem to support the possibility that the $^1D_2$ or $^3D_2$ states could be metastable. However, the evidence here is much less conclusive.

It is less probable that any of the other states belonging to this configuration are metastable. It can be shown that all of these states have strongly allowed radiative transitions to lower states, or are perturbed by configuration or spin-orbit interaction by other states which have such transitions.

USE OF THE ALKALI METALS AS DETECTORS FOR METASTABLES

According to theoretical arguments given by Hagstrum,[5] Na would be expected to have a relatively high yield for the low-lying metastable states of mercury. This is verified by experiment (Fig. 2). The conduction band of Na extends from 2.3 to 5.3 v below the vacuum level.[6] A $^3P_2$ metastable has sufficient energy (5.4 ev) to eject any of the conduction electrons. By these arguments the alkali metals, by virtue of their narrow electronic bands, should be superior for detecting metastables of low energy. Table I gives the depth of the *bottom* of the conduction band of the alkalies,[6] and therefore the lowest metastable excitation energy for which these metals would be most useful. It should be noted that this minimum energy is considerably greater than the work function, which is the depth of the *top* of the conduction band.

ACKNOWLEDGMENT

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[5] H. Hagstrum (private communication).

[6] Band levels are taken from reference 3, from H. W. B. Skinner, *Reports on Progress in Physics* (The Physical Society, London, 1939), Vol. 5, p. 257, or from theoretical calculations given in *C. Kittel, Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), second edition.