DETECTION OF LONG-LIVED EXCITED IONS OF INERT GASES AND MERCURY

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It was found that during the electron ionization of neutral Hg, Xe, Kr, Ar, and Ne atoms various excited singly, doubly, and triply charged ions (in the case of He, singly charged ones only) were formed with lifetimes $T \gtrsim 10^{-6}$ sec. From the appearance potentials of these ions, it was concluded that the excited ions were formed in states close to their subsequent ionization states. The ion excitation energy was determined by the method of secondary ionization of these ions.

1. INTRODUCTION

WHEN investigating plasma in various astrophysical and ionospheric phenomena, it is interesting to know the conditions of formation and the average lifetimes of excited ions obtained when neutral atoms are ionized by electrons. The formation of various metastable ions has been deduced from the forbidden lines in astronomical spectra.[1] Under laboratory conditions, the metastable states of neutral atoms have been the main subject of investigations,[2] and there have been far fewer studies of metastable ions. In some work[3], fairly strong intensities of the forbidden lines of singly charged ions have been observed in low-pressure discharge tubes. The concentrations of metastable states have been determined by the optical methods of absorption and anomalous dispersion.[4]

Novick et al.[5] investigated the excitation function of the metastable state $2^2S_{1/2}$ during the ionization of helium by electrons. The transition $2^2S_{1/2} \rightarrow 2^2P_{1/2}$ was induced by microwave irradiation of metastable He^+ ions; ultraviolet photons emitted in the subsequent transitions to the ground state of the He^+ ion were recorded by a photoelectric detector. Lindholm[6] showed that during the ionization of atoms by means of electrons, atomic ions are more likely to be formed in the various lower metastable states. Some idea of the energy-state composition of a beam of such ions may be obtained by investigating the mass spectra of various molecules which exchange charge with these ions. Hagstrum[7] investigated the formation of metastable singly charged ions during the ionization of Ar, Kr, and Xe atoms. These ions were recorded using their enhanced (compared with normal ions) ability to knock out electrons from clean metal surfaces. Only recently has the formation of highly excited long-lived states of ions been recorded.

In the present work, we investigated the formation of singly, doubly and triply-charged long-lived highly-excited ions, as well as several metastable ions, during the ionization of inert gas and mercury atoms by electrons.

2. EXPERIMENTAL METHOD

The investigation was carried out using the method of intersecting ion and electron beams in a double mass spectrometer with an electron gun between two magnetic mass analyzers.[8,9] Gas atoms were ionized by electrons of energy E_1 in the ion source, giving rise to ions of various charges in the ground and excited states. The first mass analyzer directed a beam of the investigated ions through a system of slits into the ionization chamber of the electron gun. The secondary ions, formed on ionization of the primary ones by electrons of energy E_2, were analyzed by the second mass analyzer and recorded with an ion detector. The presence of excited ions in the primary beam was deduced from the value of the effective ionization cross section of these ions during the second electron impact and from the dependence of the ionization cross section on the electron energy E_1 in the ion source.

If ions of given m/e (m is the mass and e is the charge of an ion) are formed in the ion source in various excited states, the method of intersecting beams allows us to detect the levels or groups of levels which are most likely to be excited. For this purpose, we need to determine experimentally: a) the appearance potentials E_{1p} of the excited ions resulting from the ionization of neutral atoms in the ion source; b) the appearance potentials E_{2p} of the secondary ions produced during the second electron-impact ionization of the primary ions, obtained from the ion source when the electron energy is $E_1 < E_{1p}$ and $E_1 > E_{1p}$. Since the ionization of ions in the electron gun takes place $\approx 10^{-6}$ sec after the formation of the primary ions, our method records the excited ions having lifetimes $T \gtrsim 10^{-6}$ sec, i.e., the long-lived excited ions. These ions may be: 1) metastable ions for which the electric dipole transition to the ground level is forbidden by various selection rules; 2) ions excited to states with high quantum numbers. In the latter case, it is more likely that only one of the ion electrons will be excited. This may be established as follows. For two-electron excited states to exist, we need many selection rules which would forbid the excited electrons to occupy vacancies in the lower levels. Moreover, the lifetimes of two-electron excited states are shorter because of the interaction between two excited electrons.[10]

An excited ion may be long-lived if its one-electron excitation is associated with a high principal quantum number. Obviously, the energy levels of such an ion lie close to the ionization limit. The outer electron is then in a field which is nearly Coulomb in type, and consequently the ion may be considered to be hydrogen-like.[11] The validity of this approximation is greater for strongly excited ions. As is known,[12] the lifetimes of the quantum states of the hydrogen atom and hydrogen-like ions increase with increase of the principal quantum number. It should be noted that at a given excitation energy the principal quantum number has its maximum value when only one electron is excited in a many-electron system. These arguments lead us to assume that highly excited states are long-lived ones if they are associated with high principal quantum numbers.

We shall point out some differences between the cross sections for the loss of one and more than one electrons in the case of the ionization of ions with one and two excited electrons. At a given excitation energy, the cross section for the one-electron loss should be higher in the former case than in the latter. In the former case, the influence of excitation on the cross section for the one-electron loss will be greater than on the cross section for the loss of several electrons.

As will be shown below, these assumptions are justified experimentally. Moreover, the probability of ion formation in the ionization of atoms by electrons is higher in the one-electron excitation case than in the case of two-electron excitation.

Thus, we may assume that highly-excited long-lived ions are mostly ions with one excited electron, rather than ions with a large number of excited electrons.

It has been shown earlier[8,9] that in investigations of the processes of the ionization of primary ions B^{n+} (B^{n+} denotes the investigated ions of charge $n = 1, 2, 3$) by electrons

$$B^{n+} + e \rightarrow B^{(n+1)+} + 2e \qquad (1)$$

we have detected a background of $B^{(n+1)+}$ ions only, i.e., ions which have lost only one electron. Other background lines have not been detected although the ion detector sensitivity would have allowed the measurement of ion currents 100 times smaller than the $B^{(n+1)+}$ ion current. These secondary ions are formed from the primary ions B^{n+} in processes of the type

$$B^{n+} \rightarrow B^{(n+1)+}. \qquad (2)$$

A detailed investigation of the sources of the background has shown that the formation of $B^{(n+1)+}$ ions in accordance with Eq. (2) consists of[9] two processes: a) "stripping" of the primary ions in a gas occupying the space between the two mass analyzers, and b) ionization of the excited ions near the metal surface of the edge of a slit S_1. The reaction (2) proceeds by both these processes simultaneously. It is difficult to separate completely by experimental means the secondary ions formed in the cases a) and b). Therefore, the total effect is recorded. Obviously, the background due to the processes a) and b) depends in different ways on the gas pressure between the mass analyzers and on the geometry of the slits which collimate the ion beams.

In some preliminary experiments, we investigated the dependence of the intensity of the background on these factors and selected the conditions for the background to be minimal. To reduce the background due to the "stripping" of ions in the gas, we used relatively low ion-accelerating voltages (2800 V). Then, the intensity of the background depended mainly on the presence of excited ions in the beam and consequently on the electron energy E_1 in the ion source. This effect was used[13] as a second method for the study of the processes of the formation of long-lived excited ions during the ionization of neutral atoms. In investigations of the formation of excited ions by the first method [reaction (1)] it was necessary to use low electron energies E_2 since, at a sufficiently high constant energy E_2, the probability of the ionization of the primary ions might vary only slightly with E_1 if the content of excited ions in the primary beam is low. To detect the excited ions in this case, one could reduce the electron energy E_2 below the ionization energy of the primary ions in the ground state, in order to ionize only the excited ions.

However, at $E_2 < 20$ eV the electron-gun current was low and did not produce sufficient intensity of the secondary ions (compared with the background intensity). In such cases, we could use the second method for detecting the excited ions [reaction (2)] i.e., investigate the behavior of the secondary-ion current which is the background for the processes (1). As mentioned above, at ion-accelerating voltages of 2800 V, the excited ions were mainly ionized in the process (2). Therefore, when a highly sensitive detector (a type SI-01 ion counter) was used, this method allowed us to detect very small numbers of excited ions in the beam. Thus, the three methods [processes (1), (2a) and (2b)] supplemented one another and allowed us to detect long-lived excited ions. It should be noted that these methods for detecting excited ions were particularly sensitive to strongly excited states of ions.

3. RESULTS OF THE MEASUREMENTS AND DISCUSSION

The investigation of the dependence of the effective cross sections for the ionization of ions by the second electron impact on E_1, the energy of electrons in the ion source, shows that the excited-state composition of the primary ion beam depends on E_1. Figure 1 shows a typical dependence of the probability of the ionization of Xe^{2+} ions on E_1 for E_2 = const. This figure indicates that the probability of the ionization of Xe^{2+} depends on E_1 if $E_1 \geq E_{1p}$. The energy $E_{1p} = 65$ eV may be regarded as the appearance potential of the excited Xe^{2+} ions in the process of ionization of Xe atoms. Thus, the E_1 dependence of the effective cross section of the process

$$Xe^{2+} + e \rightarrow Xe^{3+} + 2e$$

in the ionization chamber of the electron gun at E_2 = const is governed by the appearance of excited ions in the process

$$Xe + e \rightarrow Xe^{2+} + 3e$$

in the ion source. Figure 1 shows that the ionization probability curve has a maximum. A beam of Xe^{2+} ions contains excited ions of various states. Therefore, we cannot say that the probability curve is a function of the excitation of a given level. The nature of the curve in Fig. 1 reflects the nature of the excitation curves of many levels and depends on them.

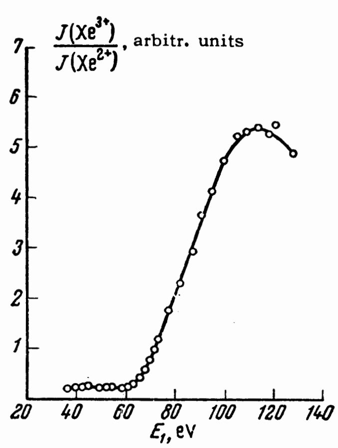

FIG. 1. Dependence of the probability of the ionization of Xe^{2+} ions at E_2 = const on E_1, the energy of the electrons in the ion source (the ordinate gives the ratio of the secondary and primary ion currents).

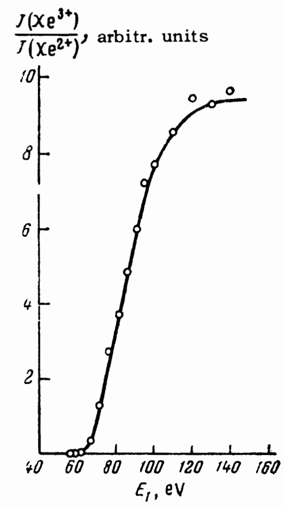

FIG. 2. Dependence, on the electron energy E_1, of the probability of the formation of Xe^{3+} ions from Xe^{2+} ions in the process (2).

Figure 2 shows the dependence of the probability of the formation of Xe^{3+} ions from Xe^{2+} ions on E_1, the energy of electrons in the ion source during the process (2). It is evident from Fig. 2 that the background, and the excited Xe^{2+} ions, appear at $E_{1p} = 65$ eV, in agreement with Fig. 1. Consequently, the presence of excited ions and their appearance potentials may be recorded by means of curves of the type shown in Figs. 1 and 2.

We investigated the formation of long-lived excited ions Hg^+, Xe^+, Kr^+, Ar^+, Ne^+, He^+, Hg^{2+}, Xe^{2+}, Kr^{2+}, Ar^{2+}, and Xe^{3+} in the ionization of the corresponding neutral atoms by electron impact. The table lists the following quantities for all these ions: the ground-state energies of B^{n+} (n

Energies of ground and metastable states of ions and experimental appearance potentials of excited ions (in eV)*

	Hg+	Xe+	Kr+	Ar+	Ne+	He+	Hg^{2+}	Xe^{2+}	Kr^{2+}	Ar^{2+}	Xe^{3+}
Ground states B^{n+}	10.43	12.13	14.00	15.76	21.56	24.58	29.18	33.34	38.56	43.38	65.42
Metastable states B^{n+}	14.83	23.96	28.90	32.16		65.38	34,49	35.44	39.79	45.06	
		24.38	29.62	33.38			34.88	37.95	42,65	47,45	
		24.45	29.86	33.45			36.41	47	55.73	61.42	
		26.37	30.39	34.25			36.73	48.95	57,87	66.32	
							41.30	49	58.45		
								49.80	58.73		
									60,28		
Ground states $B^{(n+1)+}$	29.18	33.34	38.56	43.38	62.6	78.98	61.68	65.42	75.76	84.26	110.88
E_{1p}	29	33	38	43	62	79		65			110

*For some ions, the lowest metastable levels are not listed.

= 1, 2, 3) ions investigated in the process (1); energies of various metastable excited states of B^{n+} ions; ground-state energies of $B^{(n+1)+}$ ions which are ionized one unit charge more than the investigated B^{n+} ions; and, finally, the experimentally determined appearance potentials E_{1p} of the excited B^{n+} ions. To find the values of E_{1p}, the E_1-energy scale was calibrated by means of known ionization potentials of the investigated atoms. The electron energy E_1 was determined with an accuracy of ± 0.5 eV. In the table, it is assumed that the ground-state energies of neutral atoms corresponding to the investigated ions are zero. Metastable states with the energy levels listed in the table[14] are metastable because the electric dipole transition from each level to lower levels is forbidden by Laporte's rules and by the change of J (J is the total-momentum quantum number). In the case of He^+ ions, the transition to the ground level is forbidden by the rule governing the change of L (the azimuthal quantum number). It is possible that not all the upper metastable levels of many-electron ions are listed in our table because Moore[14] found the atomic levels from the analysis of optical spectra. The table shows that the appearance potentials E_{1p} of singly, doubly and triply-charged long-lived excited ions are close to the double, triple and quadruple ionization potentials of the corresponding atoms and are considerably greater than the appearance potentials of the metastable ions listed in the table.

Similar results, some of which have been described by us earlier,[13] have been obtained in a study of the ionization of ions by the process (2). There has been a recent report[15] of the existence of long-lived highly-excited Ar^+ ions with an appearance potential (≈ 43 eV) close to the appearance potential of non-excited Ar^{2+} ions, which is in agreement with the results obtained earlier[13] and those reported here. Thus we may conclude that the ionization of atoms by sufficiently fast electrons produces long-lived excited ions with excitation energies close to the single-ionization energy of these ions. It is possible that some highly excited ions with an electron in a state of high principal quantum number are metastable, their states not having been listed by Moore.[14] Moreover, metastable ions are formed with states listed in our table. It is natural to expect that when atoms are ionized by electrons ions will be formed in excited states which are short-lived and are not recorded by the methods described in the present work.

Figure 3 shows, by way of example, the dependence of the probability of the ionization of Xe^+ ions by electrons on E_1, the electron energy in the ion source for E_2 = const. Figure 3 indicates that in the process of ionization of Xe atoms, excited Xe^+ ions belonging to two groups are formed.[1)]

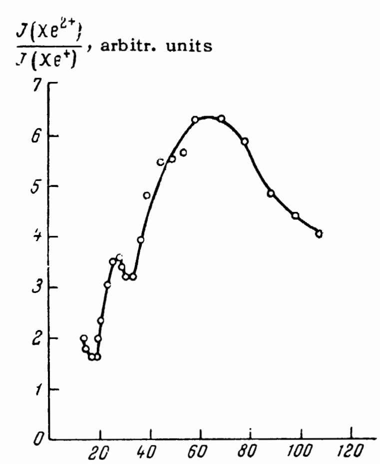

FIG. 3. Dependence of the probability of the ionization of Xe^+ ions at E_2 = const on E_1, the energy of the electrons in the ion source.

[1)]A small rise of the curve on approach to the ionization potential of Xe atoms is possibly due to metastable Xe^+ ions in the $^2P_{1/2}$ state (13.44 eV).

The first group of Xe^+ ions has an appearance potential $E_{1p} \approx 25$ eV and shows evidence of the formation of the metastable ion states listed in the table. The second group of Xe^+ ions represents long-lived highly-excited ions with $E_{1p} \approx 33$ eV. In these experiments, we investigated also the dependence on the energy E_1 of the probability of loss of two electrons. As expected, a change in the energy E_1 affected this case much less than the case of one-electron loss. Thus, this result agrees with the assumption that the excited states of ions are of the one-electron type.

Moore[14] did not list "metastable" (in the sense given above) states for Ne^+ ions. We[9] concluded that the formation of metastable Ne^+ ions with lifetimes $\approx 10^{-5}$ sec, capable of altering considerably the cross section for the ionization of these ions by electron impact, is not very likely. Investigation of the dependence of the Ne^{2+} ion yield in the process of "stripping" Ne^+ ions by gas atoms and by ionization at the edges of the slit S_1 indicated the formation of excited Ne^+ ions near the double-ionization potential of Ne atoms (cf. the table).

Figure 4 shows the dependence of the current of secondary Ne^{2+} ions, formed in the process (2), on E_1, the energy of electrons in the ion source. The same figure gives the dependence of the primary Ne^+ ion current on E_1. It is evident from Fig. 4 that long-lived highly excited Ne^+ ions are formed.

Apart from ions with filled p-shells, our table lists Hg^+, Hg^{2+}, and He^+ ions. Moore[14] lists for Hg^+ the state $^2D_{5/2}$ (14.83 eV), which may be regarded as metastable. The states of Hg^+ with higher energies, listed by Moore,[14] are characterized by strong jj-coupling.

Figure 5 shows the dependence of the ionization probability $J(Hg^{2+})/J(Hg^+)$ of Hg^+ ions on the

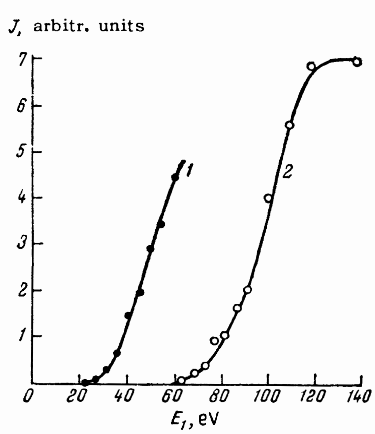

FIG. 4. Dependence of the ion currents on E_1, the energy of the electrons in the ion source: 1) current of primary Ne^+ ions; 2) current of secondary Ne^{2+} ions from the process (2).

electron energy E_1 for E_2 = const. It is evident from Fig. 5 that the appearance potential $E_{1p} = 29$ eV of long-lived excited ions is considerably greater than the energy of the $^2D_{5/2}$ state. Thus, Hg^+ ions also have highly excited long-lived states. The formation of Hg^+ ions in the metastable state $^2D_{5/2}$ was mentioned by Moore[14] and Wilmenius and Lindholm.[16] It is probable that the primary ion beams in our experiments also contained Hg^+ ions in this state.

The appearance potential E_{1p} of excited He^+ ions is higher than the energy of the metastable state $2^2S_{1/2}$. In this case, He^+ ions are obviously formed in excited states with high principal quan-

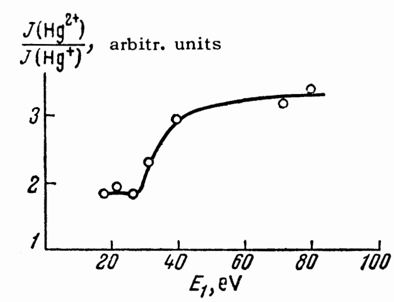

FIG. 5. Dependence of the probability of the ionization of Hg^+ ions at E_2 = const on the electron energy E_1.

tum numbers. This is in agreement with the theoretical prediction that in one-electron systems the lifetimes of excited states with high quantum numbers should be long.[12] In this connection, we may assume that one-electron excitations are also responsible for the formation of long-lived highly-excited many-electron ions (cf. the table). By analogy with one-electron systems, the one-electron excited states of many-electron ions should have high quantum numbers.

From our results on the formation of highly-excited long-lived ions and from other published data,[11,12] we would expect that the impact of sufficiently energetic electrons on atoms would give rise to highly excited atoms. These excited atoms, being hydrogen-like (one of the electrons is in a state with a high principal quantum number), should be long-lived.

In conclusion, we shall discuss the problem of the probabilities of the formation of ions in long-lived excited states. It is evident from our work that the appearance potentials of the long-lived highly-excited B^{n+*} ions are close to the appearance potentials of the non-excited ions $B^{(n+1)+}$, whose charge is one unit larger. Since the energy thresholds of the processes

$$B + e \rightarrow B^{n+*} + (n+1)e, \tag{3}$$

$$B + e \rightarrow B^{(n+1)+} + (n+2)\,e \qquad (4)$$

are close and the number of states of the excited B^{n+*} ions near the appearance potentials of the $B^{(n+1)+}$ is large, we can expect—from general physical considerations—that when atoms are ionized by electrons the effective cross sections $\sigma(B^{n+*})$ for the formation of the B^{n+*} ions and the cross sections $\sigma(B^{(n+1)+})$ for the formation of the $B^{(n+1)+}$ ions should be of the same order. The content of the excited B^{n+*} ions was estimated by two methods. In the first method, we used the results of measurements of the effective cross sections for the ionization of ion beams containing or free of excited ions by electrons. In the second method, we used the results of measurements of the effective cross sections for the processes of ion stripping by gases. The values of the relative fractions of excited ions α, found by these methods, agreed to within a factor of 2—3. In beams of the investigated ions the maximum values of α for long-lived highly excited ions were approximately within the limits 0.2—2%. Rough estimates allowing for the loss of the excited B^{n+*} ions in beams indicated that the cross sections $\sigma(B^{n+*})$ in the process (3) and $\sigma(B^{(n+1)+})$ in the process (4) are quantities of the same order.

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