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Field ionization of excited states of potassium

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We have studied the electric field ionization of excited states of K and have found that it is similar in its gross features to the field ionization of Na. However, there are clear differences which are particularly important for applications. We attribute the differences to the coupling of states of different $|m_l|$ in high electric fields by the spin-orbit interaction of the K p states.

I. INTRODUCTION

Field ionization of atomic Rydberg states is currently being studied both for the intrinsic interest[1] in the process and for the potential applications such as spectroscopic[2-4] and collision studies.[5,6] Since most such studies involve the zero-field angular momentum states, a detailed understanding of how these states are ionized by a pulsed electric field is important for these applications. We have previously carried out experiments to characterize the pulsed field ionization of excited Na, which have led to a simple physical model of the processes.[7,8] The model is based upon an adiabatic uncoupling of $\overline{L}$ and $\overline{S}$ in passing from low to intermediate field followed by an adiabatic passage of the $|m_l|$ states to the high ionizing field disregarding the valence electron's spin. Here we describe recent experiments with K in which we have found that the spin-orbit coupling is important even in high fields, leading to a more complicated field ionization behavior.

II. EXPERIMENTAL APPROACH

The beam apparatus and method used in these experiments have been described in detail elsewhere,[7] so we shall only briefly describe them here. An atomic beam of K passes between a plate and a grounded grid, where it is excited by two pulsed tunable lasers from the $4s_{1/2}$ state to the $4p_{1/2}$ or $4p_{3/2}$ state and then to a high s or d state (or to the s or d component admixed to another state by an electric field). After the laser pulses a positive high-voltage pulse is applied to the plate, field ionizing the atoms and accelerating the ions formed into a particle multiplier. The resulting signal is then put into a boxcar averager.

The ionization threshold fields for the s, p, and d states were measured by measuring the total (time integrated) ion current while sweeping the magnitude of the ionization pulse. The ionizing field remains within 3% of its peak value for 200 ns and then decays, so the ionization thresholds we observe correspond to an ionization rate of $\sim 10^7\ s^{-1}$. A typical ionization threshold measurement of the $20d_{3/2}$ state is shown in Fig. 1(a). As Fig. 1(a) indicates it is difficult to clearly distinguish the thresholds which occur at higher fields because of the presence of the signal from the lower field thresholds. To make the higher-field thresholds more apparent we have used the inherent time resolution of our field ionizer. Although the rise time from 10% to 90% of our ionizing field pulse is ~300 ns, the final 10% requires

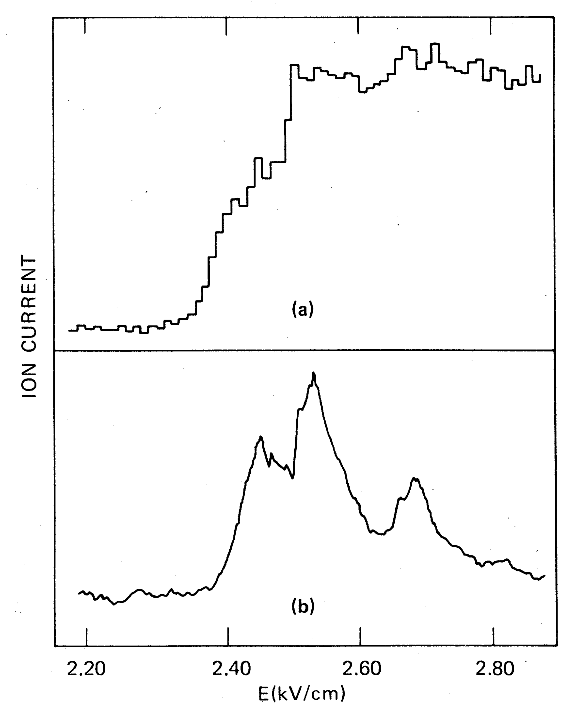

FIG. 1. Ionization thresholds of the K $20d_{3/2}$ state. (a) Total ion current vs ionizing field. There are three thresholds at 2.40, 2.50, and 2.68 kV/cm. (b) Time-resolved ionization current vs ionizing field using a 40-ns wide gate, illustrating the higher-field thresholds clearly.

100 ns, which is ideally suited to time-resolved detection of ionization thresholds which are separated by about 5%. To do time-resolved detection we use a 40-ns wide boxcar averager gate and again sweep the magnitude of the ionizing field pulse. The position of the boxcar averager gate is chosen so that we detect atoms which are ionized only at the peak of the ionization pulse. Those atoms which have lower ionization thresholds produce an ionization signal earlier than the boxcar gate and are not observed. In Fig. 1(b) we show the ionization signal of the $20d_{3/2}$ state time resolved in this way. Note that all the thresholds are clearly resolved. Although it is difficult to make precise measurements of the ionization thresholds using the time-resolved approach because the apparent threshold field depends upon the temporal position of the boxcar gate, the method is very useful in applications such as radio frequency resonance experiments[3,9] and superfluorescence studies[10] not requiring absolute threshold field information.

To measure the ionization thresholds of the higher l states, $f, g, h, \ldots,$ which we term the manifold states, we have employed a new method which is much easier than measuring the threshold for each state. We excite the atoms in a field of 357 V/cm (in which the states of the manifold are separated enough to be resolved by the laser) and then apply the pulsed ionizing field. We make a wavelength sweep across the manifold for each of a series of values of pulsed ionizing field starting with an ionizing field strong enough to ionize all the states under study. As we progress to lower ionizing fields we observe how each of the levels disappears. This gives us the same information as locating each state and measuring its threshold. To verify this we recorded the thresholds of several manifold states in the manner used to record the thresholds of the s, p, and d states and found the thresholds to be in excellent agreement with the results obtained by the new approach.

III. RESULTS AND DISCUSSION

Before presenting the detailed K results it is worthwhile to briefly review the results obtained with Na.[7] In the field ionization of Na s, p, and d states we observed a number of thresholds equal to the number of possible $|m_j|$ states (in an electric field the sign of the magnetic quantum number is not important). For example, for a $d_{3/2}$ state we observed two thresholds and for a $d_{5/2}$ state we observed three thresholds.

To discuss how the atoms pass from zero field to the high ionizing field, it is convenient to define three field regimes. In the low-field regime the Stark effect is small compared to the fine-structure (fs) intervals, and J and m_j are the "good" quantum numbers. In the intermediate-field regime the Stark effect is greater than the fine-structure intervals but less than the separation between n states. In this regime m_l and m_s are the "good" quantum numbers. In the high-field regime the Stark effect is greater than the separation between n states, and again m_l and m_s are the "good" quantum numbers.

In the field ionization of Na the atoms pass adiabatically from the low-field J, m_j states to the intermediate field m_l, m_s states. Each $|m_l|$ state then passes adiabatically to the high ionizing field; that is, there are no crossings with other states of the same $|m_l|$ because of the nonzero quantum defects δ, of the Na s, p, and d states which couple states of different n. At the highest n states we studied we observed multiple $|m_l|=2$ thresholds, indicating the onset of partially diabatic behavior, which we attribute to the small size of the Na d quantum defect. For reference the Na and K quantum defects derived from Moore's tables[11] are given in Table I. Note that for Na the effect of the valence electron's spin is ignored in the passage from intermediate to high field. This is equivalent to assuming that all spin-orbit couplings are relatively small in high field and that the passage from intermediate to high field is diabatic with respect to $|m_j|$.

In these experiments with K the gross features are similar to those of Na, but three features were observed which are quite different than those we observed with Na. First, we observed multiple thresholds for the s states. Second, the fine-structure states for both p and d states appear to have identical field ionization behavior, within the resolution of the experiments. That is, the number of ionization thresholds did not equal the number of $|m_j|$ states but was the same for both $d_{3/2}$ and $d_{5/2}$ states, for example. Finally in the p and d states there were multiple $|m_l|=0$ and 1 thresholds but never any multiple $|m_l|=2$ thresholds (which we had seen in Na).

The observed thresholds are listed in Table II and are labeled by the high-field $|m_l|$ state. For the s and p states $|m_l|$ is of course 0 or 1. The $|m_l|=2$ states were identified by populating the ex-

TABLE I. Quantum defects of K and Na. [a]

l	Na	K
s	1.35	2.10
p	0.85	1.70
d	0.015	0.27

[a] See Reference 11.

TABLE II. K threshold fields for ionization (fields required to produce an ionization rate of $10^7 s^{-1}$, in kV/cm uncertainties are ±3%).

State	$\lvert m_l \rvert = 0, 1$	$\lvert m_l \rvert = 2$
17*s*	7.46, 7.58, 7.73, 7.88	
18*s*	5.65, 5.83, 6.00, 6.12	
19*s*	4.42, 4.55	
20*s*	3.58, 3.79	
21*s*	2.85, 2.93, 3.04	
22*s*	2.34, 2.37, 2.43	
18*p*	4.54, 4.76, 4.91	
19*p*	3.62, 3.86	
20*p*	2.90, 2.96	
21*p*	2.39, 2.53	
22*p*	1.92, 2.01	
15*d*	7.56, 7.81	8.57
16*d*	5.80, 5.96, 6.14	6.47
17*d*	4.60, 4.73, 4.91	5.04
18*d*	3.61, 3.71	4.02
19*d*	2.95, 2.99, 3.13	3.30
20*d*	2.40, 2.50	2.68

cited *d* states in a weak dc field and polarizing the laser so that $\bar{E}_{\text{laser}} \| \bar{E}_{\text{dc}}$ to eliminate the highest $\lvert m_j \rvert$ component and therefore those states which go to $\lvert m_l \rvert = 2$ states in high field. With $\bar{E}_{\text{laser}} \| \bar{E}_{\text{dc}}$ we found that the thresholds labeled $\lvert m_l \rvert = 2$ in Table II completely disappeared for both the $d_{3/2}$ and $d_{5/2}$ states. In Table II we have grouped the $\lvert m_l \rvert = 0$ and 1 thresholds together because it is impossible to make further assignment of the $\lvert m_l \rvert = 0$ and 1 thresholds [recall that the K $20d_{5/2}$ threshold looks *identical* to the $20d_{3/2}$ threshold of Fig. 1(a)].

The most probable cause of the differences between Na and K is the larger spin-orbit coupling of the *p* states in K. In Table III we list fs intervals for Na and K states nearest $n^* = 16$, where $n^* = n - \delta$. Let us consider for a moment the two extremes of *LS* coupling corresponding to very small and very large fine-structure intervals. For Na, with small fs intervals, there is very little coupling between m_l and m_s in the intermediate- and high-field regimes so that the valence electron's spin is irrelevant to the problem. In this case states of different $\lvert m_l \rvert$ but the same $\lvert m_j \rvert$ are virtually uncoupled and are free to cross each other. Thus, as stated earlier, the passage through the high-field regime is diabatic with respect to $\lvert m_j \rvert$. Littman[12] has pointed out that in the heavier alkali metals, Cs in particular, with large *p* fine-structure intervals, the coupling between levels of $\lvert m_l \rvert = 0$ and 1 states is strong even in high fields. In the limit of very strong spin-orbit coupling, or equivalently when the *p* fine-structure intervals are large enough, the passage will be adiabatic passage with respect to $\lvert m_j \rvert$, the opposite of the situation in Na.

For the case of moderate *p*-state fine structure, the high-field passage will be partially adiabatic with respect to $\lvert m_j \rvert$, which is manifested experimentally by such features as those which we mentioned earlier as being different from Na. Thus we feel that most of the differences between the field ionization of Na and K are due to the partially adiabatic passage of K through the high-field regime with respect to $\lvert m_j \rvert$.

We can easily make a quantitative estimate of whether or not it is feasible that the K *p* fs intervals can lead to partially adiabatic and partially diabatic passage with respect to $\lvert m_j \rvert$ through the high-field regime. Consider for a moment the field regime of ~2 kV/cm, where the 16*d* state intersects the highest state of the $n = 15$ manifold as shown by Fig. 2. The Stark shifts of these two levels are, respectively, ∓450 MHz/(V/cm) for both K and Na. For K, the case shown, the fs interval Δ of the nearest *p* state 17*p* is 6.3 GHz and the coupling at the crossing of the two states is $k\Delta$, where $0.05 < k < 1$ depending on the amount of *p* character in the Stark levels. Figure 2 is drawn for $k = 0.1$, a typical value. If the crossing is traversed in a time τ such that $k\Delta\tau \ll 1$, the passage will be diabatic and if $k\Delta\tau \gg 1$ the passage will be adiabatic. When the amplitude of the ionization pulse is set to ionize the 16*d* state, at a field of 2 kV/cm the slew rate of the field is 10^9 V/cm s. Thus for the K level crossing shown in Fig. 2 the time to traverse the crossing τ equals 3 ns. When this is combined with a typical splitting of 0.1Δ, 630 MHz, we find that $k\Delta\tau = 1.89$. In this

TABLE III. Na and K*p* and fs intervals Δ, and tensor polarizabilities α_2, near $n^* = 16$.

	Na			K	
	Δ (GHz)	α_2 [MHz/(V/cm)^2]		Δ (GHz)	α_2 [MHz/(V/cm)^2]
16*p*	1.55 [a]	0.022 [a]	17*p*	6.3 [b]	~0.01
16*d*	−0.023 [a]	−1.47 [a]	16*d*	−0.306 [c]	−0.0315 [c]

[a] See Reference 4.
[b] See Reference 11.
[c] See Ref. 9.

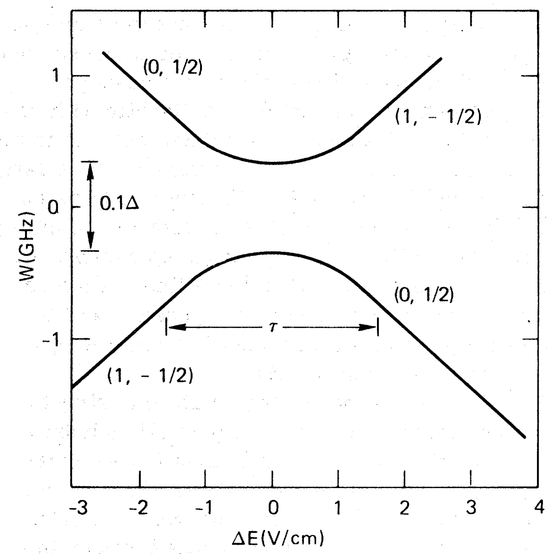

FIG. 2. Level crossing between the lowest state of the K $n=16$ manifold and the highest state of the $n=15$ manifold at ~ 2 kV/cm showing the coupling between the $|m_l|=0$ and $|m_l|=1$ levels produced by the $17p$ state spin-orbit coupling. The states are labeled (m_l, m_s). Δ is the $17p$ fs interval and τ is the time required for the field to change as shown by the arrow.

case the level crossing will be traversed partially adiabatically and partially diabatically with respect to $|m_j|$. For the analogous crossing in Na $0.1\Delta = 155$ MHz and $\tau = 0.75$ ns so that $k\Delta\tau = 0.119$

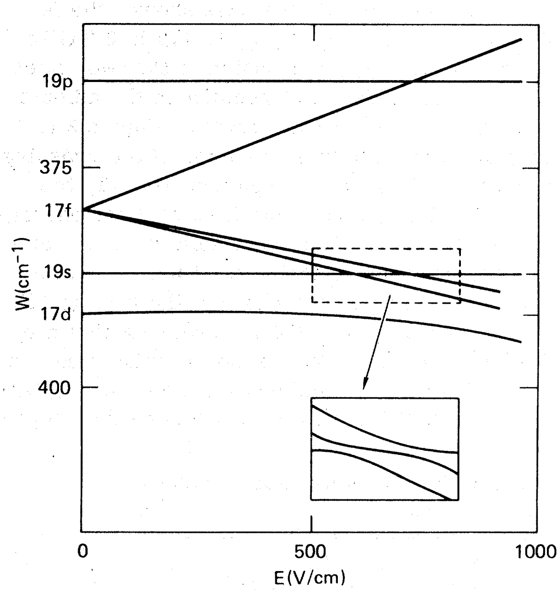

FIG. 3. Energy-level diagram in the intermediate-field regime showing the intersection of the $19s$ and $19p$ states with the $n=17$ manifold states. The inset is an expanded view of the region outlined by the broken lines showing the adiabatic paths followed by the atoms in the low- to high-field passage.

and crossing is likely to be traversed diabatically with respect to $|m_j|$. Thus it seems to be quantitatively likely that the K p fs couples $|m_l|=0$ and 1 states leading to partially adiabatic and partially diabatic passage with respect to $|m_j|$ in the field ionization of K (but not of Na).

Let us now return to the previously mentioned differences between K and Na and show how the partially adiabatic high-field passage of K with respect to $|m_j|$ is consistent with the experimental observations. Consider the multiple thresholds of the K s states. Strong spin-orbit coupling would lead to s states' ionizing via both the $|m_l|=0$ and $|m_l|=1$ states which are coupled in high field via $|m_j|=\frac{1}{2}$. The energy dependence of the K levels in an electric field, as shown in Fig. 3, suggests an alternative explanation for the multiple s thresholds, namely, partially diabatic passage through the intermediate-field regime with respect to $|m_l|=0$. As shown by Fig. 3 the most likely place for this to occur for the $19s$ state, for example, is where the $19s$ state intersects the $n=17$ manifold of $l \geq 3$ states at 400 V/cm, long before either the $19p$ or $17d$ states are significantly mixed with the manifold states. Consequently the manifold states have very little p character and might be coupled so weakly to the $19s$ state that the $19s$ level crossings at 400–700 V/cm would be traversed diabatically with respect to $|m_l|=0$. To check this we excited the $19s$ and the first few manifold states at fields of 357, 625, and 777 V/cm, that is, on both sides of the level crossings, so that we could determine the paths the atoms followed through the crossing region. By using the ionization threshold field as a label we were able to determine that the atoms follow adiabatic paths as shown by the inset of Fig. 3. Thus partially diabatic traversals of intermediate-field crossings is not the source of the multiple s state ionization thresholds.

Unlike Na in K the p and d fs states appear identical, and have multiple $|m_l|=0$ and 1 thresholds. A partially adiabatic passage with respect to $|m_j|$ through the high-field regime would mix the $|m_l|=0$ and 1 levels and produce more thresholds, the number depending upon the number of crossings traversed in a partially adiabatic fashion. This, of course, is precisely what we have observed.

It is worth considering for a moment an alternative explanation for why the K fs states are indistinguishable in field ionization, namely, that the passage from the low field to intermediate field is partially diabatic. While this would make the two fs states indistinguishable in field ionization, it would not in any case lead to more than three thresholds for a d state and we typically observe four. Further evidence that this is not important is the fact that the $|m_l|=2$ states are *not* mixed

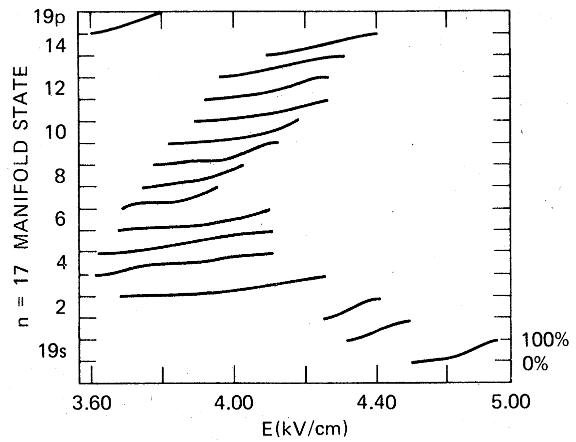

FIG. 4. Plot of the $n=17$ manifold state thresholds numbered in order of increasing energy, i.e., 1 corresponds to $17f$. The probability of ionization for each state is plotted vs electric field as shown by the scale on the right-hand side for the 19s state. During the laser excitation atoms were in a dc field of 357 V/cm and the field plotted here is the sum of the dc field and the pulsed ionizing field.

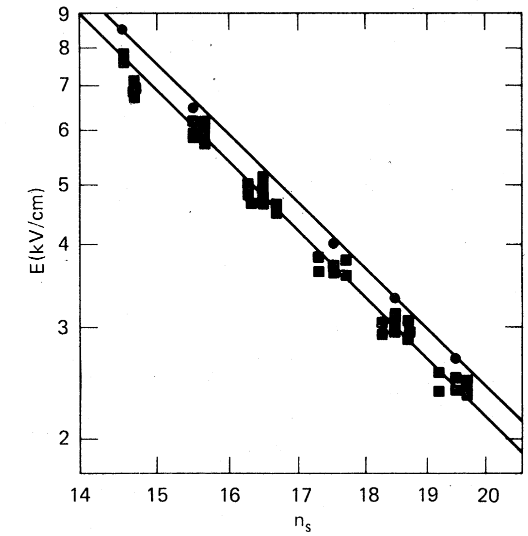

FIG. 5. Logarithmic plot of threshold ionizing field vs n_s for $|m_l|=0$ and 1 states (■) and $|m_l|=2$ states (●). The lines indicate the n_s^{-4} dependences of the threshold fields for these two sets of points.

with the $|m_l|=0$ and 1 states. Finally, whether the passage from low to intermediate field is adiabatic or diabatic for a given n level depends on the fine-structure interval Δ and tensor polarizability α_2 of the state under consideration. The field E_0 at which m_s and m_l are uncoupled is given by $E_0 = |\Delta/\alpha_2|^{1/2}$. As shown by Table III for K the d fs is an order of magnitude larger than the Na d fs and the polarizability is an order of magnitude smaller so it is inconceivable that with an identical ionization pulse the low-to-intermediate-field passage could be diabatic with respect to $|m_j|$ for K since it is adiabatic for Na.

For completeness we measured the ionization thresholds of the K $n=17$ and $n=18$ manifold states using the method described in Sec. II. In Fig. 4, we show the $|m_l|=0$ and 1 thresholds observed for the $n=17$ manifold. The analogous plot for $n=18$ is virtually identical. Note that some of thresholds appear to be very gradual, requiring a change of 10% in the field. This is simply a reflection of multiple (~4) thresholds at slightly different fields since single thresholds occur over a change of 2%–3% in field. Again, this is presumably due to spin-orbit mixing of $|m_l|=0$ and 1 states in high field. Note that there is not the expected smooth decrease in threshold field with binding energy, which we do not at this point fully understand.

IV. CONCLUSION

Although K and Na differ in their field ionization behavior due to the larger spin-orbit interaction of K, it is worth comparing the gross features of their field ionization behavior. Previously we pointed out that Na atoms pass adiabatically with respect to $|m_j|$ from low field to intermediate field and adiabatically with respect to $|m_l|$ from intermediate field to the high ionizing field, where they are ionized by a field $E=E_0(m_l)n_s^{-4}$. Here n_s is the effective Stark quantum number such that the binding energy at ionization W is given by $W=-1/2n_s^2$.

We can also apply this model to K to see how well it fits the data. As suggested by Fig. 3 the K ns, np, and nd states go to high-field Stark states with quantum numbers given approximately by

$$nd \rightarrow n_s = n - 0.50\,,$$
$$ns \rightarrow n_s = n - 2.45\,,$$
$$np \rightarrow n_s = n - 1.55\,.$$

In Fig. 5 we show the ionization thresholds plotted versus n_s^4, and the $|m_l|=0,1$ and $|m_l|=2$ points may be fit by

$$E=E_0 n_s^{-4}\,,$$

where for $|m_l|=0,1$ $E_0=3.4(2)\times10^9$ V/cm and for $|m_l|=2$ $E_0=3.9(2)\times10^9$ V/cm in good agreement with the previous results for Na. Thus in K the effect of the large spin-orbit coupling is to blur the resolved $|m_l|$ thresholds observed in Na without affecting the gross features of the field ionization behavior.

As detailed studies are made of heavier alkali-metal atoms the much larger fine-structure intervals should play an important role, and we expect that in Cs, for example, the high-field passage may be even wholly adiabatic with respect to $|m_j|$.

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