

Electron detachment in Na^- , K^- —rare-gas collisions

D. Scott, M. S. Huq, R. L. Champion, and L. D. Doverspike

Department of Physics, College of William and Mary, Williamsburg, Virginia 23185

(Received 7 February 1985)

Absolute total cross sections for electron detachment have been measured for collisions of Na^- and K^- with rare gases at relative collision energies ranging from a few eV to about 200 eV. These alkali-metal anions, which are characterized by angularly correlated ns^2 electrons, are observed to be extremely stable with respect to collisional electron detachment. For the Na^- -Ne and K^- -Ar, Kr, Xe systems, the salient features of the detachment cross sections are described by a simple curve-crossing model. Cross sections for Na^- -He, Ar, Kr, Xe and K^- -He, Ne remain small ($< 0.5 \text{ \AA}^2$) throughout the energy range studied. Striking similarities are observed between the energy dependence of these detachment cross sections and that of the cross sections for projectile excitation which results from neutral-alkali-metal—rare-gas collisions.

I. INTRODUCTION

In recent years there have been numerous studies of collisions of atomic negative ions with atomic and molecular targets. A great deal of attention¹ has been focused on the collisional dynamics of the most elementary negative ion H^- . Electron detachment of H^- and D^- by rare gases has been successfully described with several theoretical models.^{2,3} These models, which are relevant for collision energies below 1 keV, have described both total and differential cross sections, as well as the observed isotope effects.²⁻⁴ These successes indicate that the detachment process for H^- and D^- is understood for atomic targets.

A logical extension of the H^- studies is the investigation of the collisional dynamics of alkali-metal anions, which are similar to H^- in that they have two s electrons outside a closed shell. Due to their mutual electrostatic repulsion, there exists some degree of correlation between these two outer electrons, and this correlation may be radial or angular in character. It is hoped that ion-beam experiments such as those described in this paper will contribute to our present understanding of the correlation effects involved in negative-ion—atom collisions.

During the past decade, several experimental groups have studied collisions of neutral-alkali-metal atoms with rare-gas targets, but very little work has been devoted to similar investigations involving alkali-metal anion projectiles. In this paper we present the results of absolute total cross-section measurements for electron detachment of Na^- and K^- by rare-gas targets for laboratory collision energies ranging from a few eV to 300 eV. To the best of our knowledge there exists no other published data for alkali-metal negative ions in this energy range.

A few experimental studies of detachment at higher collision energies do exist. Dukel'skii and Zandberg⁵ performed experiments with Na^- and K^- as well as halogen anions in collisions with He and Ar for laboratory collision energies between 300 and 1300 eV. The total cross sections for detachment of the halogen anions were found to be three to five times larger at a given energy than those for the alkali-metal anions. This result is surprising,

since the electron affinities of the halogens (near 3.5 eV) are much greater than those of the alkali-metals (about 0.5 eV). Bydin⁶ measured detachment cross sections for Li^- , Na^- , K^- , Rb^- , and Cs^- on rare-gas targets in the 600 eV to 12 keV range; those results confirm the unexpectedly low detachment cross sections of the alkali-metal negative ions.

More recently, Andersen *et al.*⁷ reported detachment cross sections for Li^- , Na^- , and K^- at collision energies of 0.5–100 keV/amu. Their results indicate that for $E/M > 2$ keV/amu, the cross sections for detachment of these alkali-metal anions by rare-gas targets are approximately the same as those of H^- when compared at the same collision velocity. They also determined that electron detachment accompanied by excitation of the alkali-metal atom is an important channel, accounting for approximately 30% of the total detachment cross section (20% in the case of Na^- -Ne). Excitation of the rare-gas target has also been observed.

Since the present studies show that the dynamics governing collisions between alkali-metal anions and rare-gas targets are similar to those involved in collisions between neutral-alkali-metal atoms and rare-gas targets, it is appropriate to comment on what has been observed for the neutral systems. Studies of collisions between neutral K and Na atoms and rare-gas targets have focused on the collision-induced fluorescence of the alkali-metal atom. For both projectiles, the measured excitation cross sections show similar behavior with collision energy. Below 50 eV, the cross sections for excitation of the projectile alkali-metal atoms are found to be very small ($< 0.01 \text{ \AA}^2$) and nearly constant.^{8,9} Above a characteristic energy (typically in the range 50–200 eV), the measured cross sections display a strong dependence on collision energy. The weak excitation at low collision energies has been attributed to a rotational coupling⁸ between the molecular ground state and the lowest excited $^2\pi$ states (i.e., between the $3s\sigma$ and the $3p\pi$ orbitals in the case of the Na-Ne). Since these $^2\pi$ molecular states correlate to a combination of $\text{Na}(3^2P)$ and rare-gas ground-state separated atoms, the proposed population of $^2\pi$ states via rotational coupling

would be reflected in the polarization of the $\text{Na } 3^2P_{3/2} \rightarrow 3^2S_{1/2}$ line. Polarization studies of the optical emission at low energies^{9,10} lend support to this model of excitation at low energies.

At higher collision energies the cross sections for excitation of the alkali-metal atom indicate that there are two other distinct mechanisms involved.^{11,12} The first process dominates the excitation cross sections near 1 keV and is attributed to a molecular curve crossing. The second process is most efficient near 20 keV and is apparently due to the direct electrostatic interaction between the alkali-metal valence electron and the rare-gas atom. Studies of the impact-parameter dependence of $\text{Na}(3p)$ excitation have supported these conclusions.^{13,14} Further evidence in support of these models comes from detailed calculations by Courbin-Gaussorgues *et al.*^{15,16} for the Na-Ne, He systems.

In what follows we will first discuss the experimental method used and then present the electron-detachment cross sections for collisions of Na^- and K^- with rare-gas targets. Cross-section measurements for collisions of these alkali-metal anions with molecular targets have also been completed. Those results are the subject of a forthcoming paper.

II. EXPERIMENTAL METHOD

The apparatus used and the technique employed in the present experiments have been described in detail previously.^{17–19} The apparatus described in Refs. 17–19 has been modified to include a high-temperature ion source (designed specifically for the production of low-energy alkali-metal anion beams) and an improved mass analyzer for the primary beam.

The ions are formed in an electric discharge in potassium- or sodium-metal vapor; the temperature of the source is maintained at approximately 350°C in order to prevent the vapor from condensing. This vapor is provided by an oven containing the alkali metal; typically, this oven is heated to approximately 250°C for potassium and 300°C for sodium. The oven is connected to the source chamber by a valve so that the filament in the source may be replaced without exposing the alkali-metal charge to air. This valve must also be heated; achieving the proper temperature gradient from oven to source chamber is critical to the successful operation of this ion source.

The negative-ion beam is extracted from the source, mass analyzed, and focused into the collision chamber. Collisions between the negative ions and the room-temperature target gas take place in an equipotential region. The detached electrons are trapped by combined electrostatic and magnetostatic field configurations which have been described previously.¹⁹ Typical beam currents within the collision region are 0.11 nA of Na^- and 0.45 nA of K^- . The maximum accelerating potential which can be applied is 300 V.

It has been observed that this ion source produces NaH^- and KH^- in addition to Na^- and K^- . In order to ensure that there are no undesired ions in the primary beam, a 90° double-focusing sector magnet with a resolving power of 100 has been employed for mass analysis.

The K^- and KH^- mass peaks are clearly resolved; the observed contamination of the K^- primary beam by KH^- is less than 1%. The Na^- beam is similarly pure. The mass analyzer is calibrated by introducing CH_3Cl into the source in order to produce ions of mass 35 and 37. The natural abundance of ^{35}Cl and ^{37}Cl (3:1) is reproduced in the relative heights of the mass peaks. These peaks are used to calibrate the magnet sector for K^- (mass 39). F^- (mass 19) produced from CF_4 is used as a reference for Na^- (mass 23). Periodic detachment cross-section measurements made with the halogen anions are always found to agree with previous data.^{17,20}

The fringe field of the sector magnet is strong enough in the region of the collision chamber to distort the magnetic field used to trap the detached electrons. Consequently, a Helmholtz pair has been used to cancel the sector magnet's fringe field in the region surrounding the collision chamber.

The laboratory kinetic energy of the primary ion beam is determined within the collision region by a retardation technique which is accurate to within 0.25 eV. The laboratory energy width of the K^- beam varies from typically 0.6 eV full width at half maximum at the lowest energy to 2 eV at the highest energy. The energy width of the Na^- beam is about twice that of the K^- beam.

Cross sections reported here should have an absolute accuracy of $\pm 10\%$ and are reproducible to within 5%.

III. RESULTS AND DISCUSSION

The systems studied in the present work seem naturally to belong to one of two distinct categories, as determined by the energy dependence of the cross sections for electron detachment. The first category includes those systems which are characterized as having distinct thresholds for the onset of a detachment process with cross sections which exceed a few Å^2 at the highest energies studied. The energy dependence of the detachment cross sections, $\sigma_e(E)$, for these systems suggests that electron detachment above this onset energy is primarily due to a curve-crossing mechanism. The second category includes systems for which $\sigma_e(E)$ exhibits no distinct onset and remains small ($< 0.5 \text{ Å}^2$) throughout the energy range studied, indicating the absence of a curve crossing in this energy range. In the discussions which follow we will first present the detachment measurements for those systems which show a distinct onset behavior in $\sigma_e(E)$ and then follow with a discussion of the systems which fit into the second category.

A. Systems for which $\sigma_e(E)$ exhibits an onset

Total cross sections for electron detachment $\sigma_e(E)$ for collisions of Na^- with Ne are shown in Fig. 1 as a function of relative collision energy (E_{rel}). The remarkable feature of these measurements is that Na^- , with its small electron affinity ($E_A = 0.546 \text{ eV}$), is extremely stable against collisional detachment for relative collision energies up to one hundred times the E_A of sodium. This behavior is typical of systems which belong to this first category. The features exhibited by the cross section in Fig. 1 are understood qualitatively with the aid of a

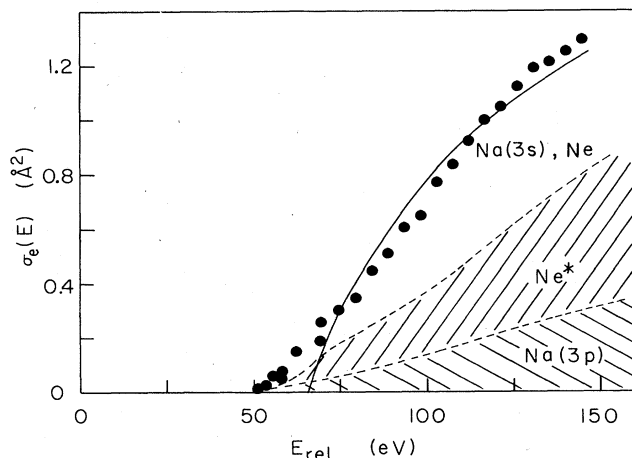


FIG. 1. Total cross sections for electron detachment in Na^- -Ne. The solid line shows the result of the fitting procedure described in the text. The shaded regions indicate the branching ratio between target and projectile excitation in collisions of the neutral system. When compared with the detachment measurements, the shaded regions indicate the relative importance of the three detachment channels (see text).

curve-crossing model. Figure 2 shows a schematic diagram of the potential energies of various states of the reactants and products which are relevant to these collisions. This diagram has been inferred in part from calculations by Courbin-Gaussorgues *et al.*¹⁵ for the Na-Ne system and also from the results shown in Fig. 1. If the incoming Na^- -Ne state remains approximately parallel to and slightly below the $X^2\Sigma^+$ continuum of $\text{Na} + \text{Ne} + e$, then the detachment probability will remain small until the crossing *A* is reached. The crossing at *A* (with coordinates R_x, V_x defined below) accounts for the onset of electron detachment at that collision energy.

Within this curve-crossing formalism, electron detachment can be described by a simple model. In this model it is assumed that the probability for detachment is zero for

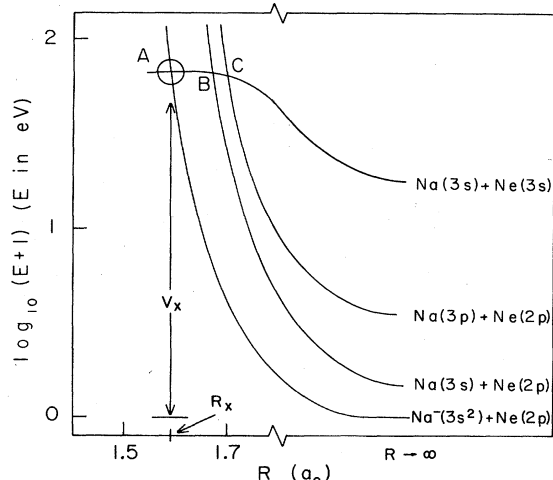


FIG. 2. Schematic diagram of the potential-energy curves of the Na-Ne- e system, including the Na^- -Ne state. The energy is measured with respect to the incoming anion-atom state.

impact parameters $b > b_x$ and is unity for $b < b_x$, where b_x is the impact parameter for which the classical turning point of nuclear motion is R_x . With this assumption, the total cross section for electron detachment is given by

$$\begin{aligned} \sigma_e(E) &= \pi R_x^2 (1 - V_x/E) \text{ for } E > V_x \\ &= 0 \text{ for } E < V_x, \end{aligned} \quad (1)$$

where V_x is the threshold energy for detachment as indicated in Fig. 2. Using this expression, a two-parameter fit was made to the detachment cross-section data for Na^- -Ne. The best fit is shown in Fig. 1 as a solid line; the parameters determined by the fitting procedure are $V_x = 65.1$ eV and $R_x = 1.59a_0$.

Although no calculations for any of the molecular states of the alkali-metal anion-rare-gas systems studied here are available, much can be inferred about these systems from what is understood about studies of the corresponding neutral-alkali-metal-rare-gas atom collisions. Calculations by Courbin-Gaussorgues *et al.*¹⁵ for the Na-Ne system indicate that excitation of both Na and Ne can be explained by a curve-crossing mechanism (see Fig. 2). These calculations show that the crossing at *B*, which is responsible for excitation of both Na and Ne, lies at an internuclear separation of approximately $1.67a_0$ and at an energy of about 64.9 eV (with respect to ground-state $\text{Na} + \text{Ne}$). The $\text{Na}(3p)$ level can be excited via a second crossing at *C*. The observed branching ratio at *C* for collisions of the neutrals⁹ yields approximately 60% Ne^* and 40% $\text{Na}(3p)$ for energies below a few hundred eV. This branching ratio is indicated by the shaded regions in Fig. 1. The fact that the three processes [detachment of Na^- by Ne; $\text{Na}(3s) + \text{Ne} \rightarrow \text{Na}(3p) + \text{Ne}$; and $\text{Na}(3s) + \text{Ne} \rightarrow \text{Na}(3s) + \text{Ne}^*$] have approximately the same threshold energy suggests that the crossing at *A*, which is responsible for electron detachment, is located near *B*. The values of V_x and R_x which are given by the fitting procedure outlined above are remarkably consistent with the calculations of Courbin-Gaussorgues *et al.*; this con-

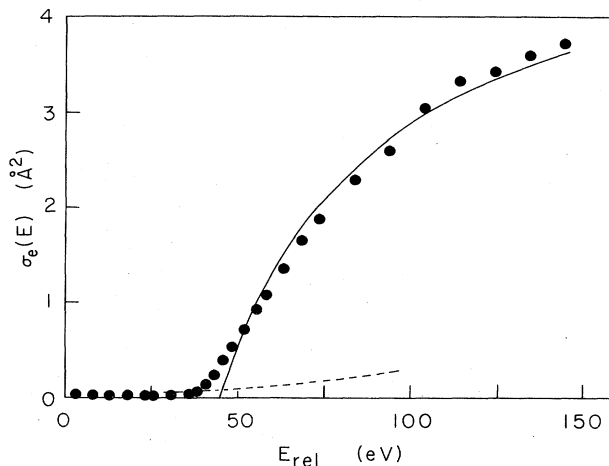


FIG. 3. Total cross sections for electron detachment in K^- -Ar (solid circles). The solid line is a fit to the data, and the dashed line represents detachment cross sections for the K^- -Ne system.

sistency lends support to the proposed model for detachment.

An estimate of the relative importance of the various detachment channels (direct detachment, detachment accompanied by projectile or target excitation) can be obtained from a comparison between the results of Mecklenbrauck *et al.*⁹ and the present measurements. If the detachment probability is indeed large for $b < b_x$ and the electron detached from Na^- is not involved in the subsequent half-collision, then the cross section for the process $\text{Na}^-(3s^2) + \text{Ne} \rightarrow \text{Na}(3p) + \text{Ne} + e$ should be approximately the same as the cross section for $\text{Na}(3s) + \text{Ne} \rightarrow \text{Na}(3p) + \text{Ne}$. With this assumption the branching ratio for the three processes mentioned above are indicated in Fig. 1 where the shaded regions show the relative importance of the three detachment channels. It appears that the branching ratios are roughly independent of energy, with detachment accompanied by projectile excitation accounting for about 20% of the total cross section. Andersen *et al.*⁷ have reported that this branching ratio is also a constant 20% in the relative energy range 10–100 keV. If the proposed branching ratios for the detachment channels at low energies are correct, then it is remarkable that the ratio for this channel (detachment with projectile excitation) is energy independent over such a wide energy range.

Three other systems studied also show features that are similar to those observed for Na^- -Ne. These systems are K^- -Ar, -Kr, and -Xe. Measurements of $\sigma_e(E)$ for these systems are plotted in Figs. 3 and 4 as a function of relative collision energy. It is interesting to note that at 35 eV, the cross section shown in Fig. 3 for K^- -Ar is approximately a factor of 160 times smaller²¹ than that for H^- -Ar. The onset for a more pronounced detachment mechanism occurs near 40 eV. The similarities between these cross sections and those of the Na^- -Ne system prompted the application of the same simple model to these systems. The results of fitting Eq. (1) to the data are summarized in Table I, and the fits are shown as solid lines in Figs. 3 and 4. Note that values for R_x increase in the order Ar, Kr, and Xe.

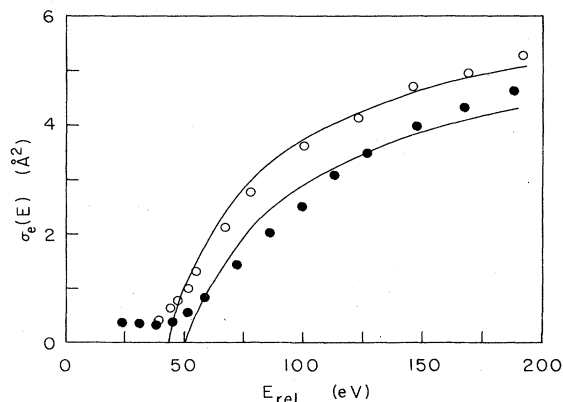


FIG. 4. Total cross sections for electron detachment in K^- -Xe (open circles) and K^- -Kr (solid circles). Solid lines indicate fits to the data.

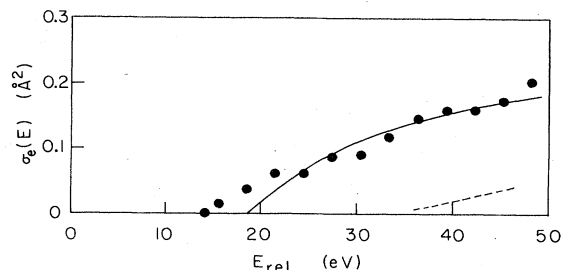


FIG. 5. Total cross sections for electron detachment in Na^- -He. The solid line is a fit to the data, and the dashed line indicates the total cross section for $\text{Na}(3p)$ excitation in Na -He collisions, estimated from Ref. 9.

Measurements of $\sigma_e(E)$ for Na^- -He are shown in Fig. 5. The presence of an apparent threshold for detachment suggested that these data could also be described by Eq. (1). The results of the fitting procedure are given in Table I, and the fit is shown as a solid line in Fig. 5. The value of R_x yielded by this procedure is unreasonably small, indicating that this system is not, in fact, described by Eq. (1). It is not clear from the present treatment of these data whether a curve crossing is involved in the detachment process for Na^- -He. For this reason this system will be reexamined in Sec. III B.

The success of the simple model outlined above suggests that a curve crossing is indeed the appropriate mechanism for electron detachment for the Na^- -Ne and K^- -Ar, Kr, Xe systems. Furthermore, it is apparent that the detachment probability at this crossing is large and may approach unity.

B. Systems for which $\sigma_e(E)$ exhibits no onset

Systems which fall into this category tend to have relatively small ($< 0.5 \text{ \AA}^2$) cross sections for energies available in these experiments. For comparison, a dashed line which represents $\sigma_e(E)$ for one of these systems (K^- -Ne) is shown along with K^- -Ar data in Fig. 3. As can be seen from the figure, the difference between the two sets of measurements is striking: in contrast to K^- -Ar, $\sigma_e(E)$ for K^- -Ne does not show any distinct threshold, and the cross section at the highest collision energy is an order of magnitude smaller for K^- -Ne than for K^- -Ar. The apparent lack of a distinct threshold implies that a curve-crossing mechanism cannot be invoked to describe the dynamics of these collisions in this energy range.

TABLE I. Results of fitting the curve-crossing model to detachment data.

System	V_x (eV)	R_x (a_0)
Na^- -Ne	65.1	1.59
K^- -Ar	45.0	2.50
K^- -Kr	50.6	2.58
K^- -Xe	42.5	2.72
Na^- -He	18.8	0.58

Measurements of $\sigma_e(E)$ are plotted in Figs. 5–8 as a function of relative collision energy for the Na^- -He, Ar, Kr, Xe, and K^- -Ne systems. No electron detachment could be observed for collisions of K^- with He in the 0.6–25 eV energy range; the upper limit to $\sigma_e(E)$ is approximately 0.01 \AA^2 . As in the case of Na^- -Ne, it is again useful to compare the present measurements of $\sigma_e(E)$ with the results of studies of the corresponding neutral systems.

The dashed lines in Figs. 5–8 indicate approximate total cross sections for excitation of the alkali-metal atom $\sigma_x(E)$ in collisions of the corresponding neutral systems. These curves have been estimated from data contained in Refs. 9 and 22. The energy dependence of these excitation cross sections is similar to that of the detachment cross sections in that there is apparently no distinct threshold for projectile excitation. A further similarity between $\sigma_e(E)$ and $\sigma_x(E)$ is that both remain small at the highest energies studied in the present work. The small values for $\sigma_x(E)$, at energies which overlap those used in the present studies, have been attributed to rotational coupling between the molecular states, as described in the Introduction. Excitation cross sections for higher collisional energies are listed in Table II and indicate that there is, in fact, a threshold for the onset of a more efficient [$\sigma_x(E) > 0.1 \text{ \AA}^2$] excitation mechanism for each of the neutral systems listed. This onset for larger values of $\sigma_x(E)$ has also been explained within the curve-crossing framework.^{8,9} Thus, it is apparent that the cross sections for alkali-metal excitation in neutral collisions remain small in Figs. 5–8 simply because the highest energies shown are not sufficient to access the crossing region. If relative collision energies up to 1 keV are considered, the $\sigma_x(E)$ curves have the same fundamental shape for all of the K, Na–rare-gas systems, suggesting that the collisional dynamics are similar for all of these neutral systems.

The striking similarity between the detachment process in Na^- -Ne and the excitation process in Na-Ne leads one to speculate about an abrupt increase in $\sigma_e(E)$ at higher collision energies for the Na^- -He, Ar, Kr, Xe and K^- -He, Ne systems. By analogy with the case of Na^- -Ne, if there were a crossing between the incoming anion-atom state and the excited-state-neutral–atom-plus-electron continuum, it could be in the vicinity of that crossing which is invoked to describe the excitation observed for

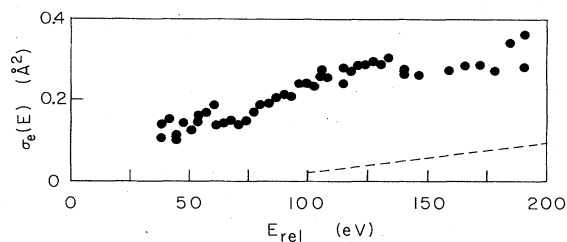


FIG. 6. Total cross sections for electron detachment in Na^- -Ar. The dashed line indicates the total cross section for $\text{Na}(3p)$ excitation in Na-Ar collisions, estimated from Ref. 9.

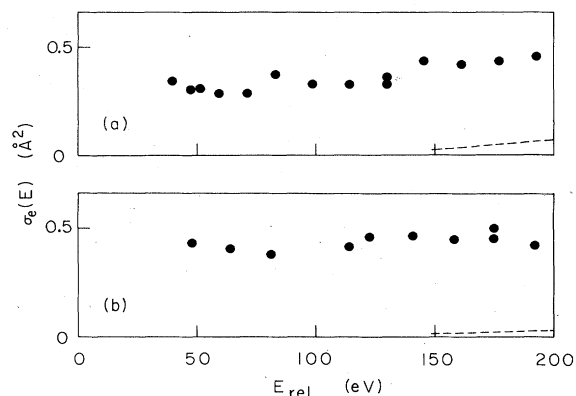


FIG. 7. Total cross sections for electron detachment in (a) Na^- -Kr and (b) Na^- -Xe. The dashed lines indicate the total cross section for $\text{Na}(3p)$ excitation in the corresponding neutral collisions, estimated from Ref. 9.

collisions in the corresponding neutral system. Following this line of reasoning, the presence of these crossings would be revealed by the energy dependence of the $\sigma_e(E)$ curves, with the onset occurring at about the same energy as for the $\sigma_x(E)$ curve. There is, in fact, some evidence for a sharp increase in $\sigma_e(E)$ for the K^- -He and Na^- -He, Ar systems. Measurements of $\sigma_e(E)$ reported by Dukel'skii and Zandberg⁵ extend down to 60 eV (E_{rel}) for K^- -He, 50 eV for Na^- -He, and 280 eV for Na^- -Ar. For the Na^- -Ar system, their lowest-energy measurement is nearly eight times greater than the present highest-energy measurement. For K^- -He, they report that σ_e is about 0.6 \AA^2 at 60 eV, whereas the upper limit for detachment up to 25 eV has been placed at 0.01 \AA^2 by the present work. Although Dukel'skii and Zandberg quote a value of $\sigma_e(E)$ for Na^- -He at 50 eV which is twice as large as that measured in the present experiment, they report such relatively large cross sections for K^- -He and Na^- -Ar that those data may be regarded as an indication of onsets in $\sigma_e(E)$. If there are indeed curve crossings which result in enhanced detachment for the Na^- -He, Ar, Kr, Xe and

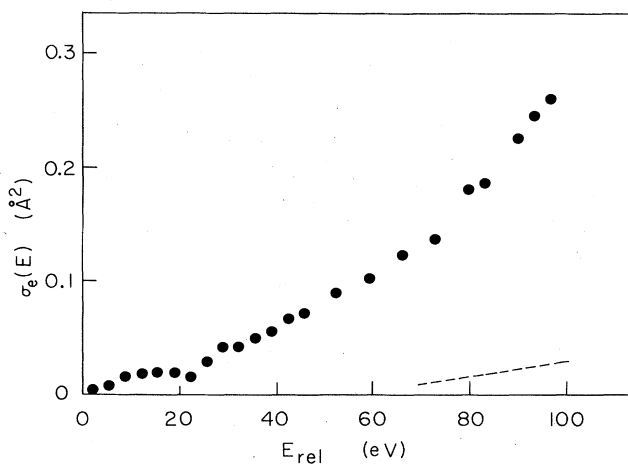


FIG. 8. Total cross sections for electron detachment in K^- -Ne. The dashed line indicates the total cross section for $k(4p)$ excitation in K-Ne collisions, estimated from Ref. 22.

TABLE II. Approximate cross sections (in \AA^2) for projectile excitation in neutral systems as a function of relative collision energy. (Estimated from Refs. 9 and 22.)

System	20 eV	60 eV	100 eV	200 eV	300 eV	500 eV
Na-He	<0.01	0.1	0.3	0.4		
Na-Ar		<0.01	<0.02	0.1	0.3	0.6
Na-Kr			0.01	0.07	0.2	0.6
Na-Xe				0.02	0.1	0.4
K-He	<0.01	0.1	0.5	1.1	1.4	1.5
K-Ne		<0.01	0.02	0.3	0.7	1.4

K^- -He,Ne systems, then it is apparent that they may be accessed by energies which lie slightly above those used in the present study.

Returning to Figs. 3 and 4, it is evident that there is a detachment mechanism which is operative at energies below V_x . The values of $\sigma_e(E)$ remain small but nonzero down to 2 eV for K^- -Ar; similar behavior of $\sigma_e(E)$ is observed for K^- -Kr. These cross sections are reminiscent of those shown in Figs. 5–8. Thus, it appears that the same detachment mechanism, one which does not involve a curve crossing, may be operative at low energies in all of the K^- , Na^- -rare-gas collisions.

These arguments lead to the suggestion that the collisional dynamics may be the same for all of these alkali-metal anion-rare-gas systems. Electron detachment appears to be governed by two distinct mechanisms. The first one is operative starting at low energies and yields cross sections which are small ($<0.5 \text{\AA}^2$). The second mechanism appears to involve a curve crossing and exhibits an onset at moderate energies (50–200 eV). Both of these mechanisms are evident in the present measurements for the K^- -Ar,Kr systems. It is noteworthy that a similar energy dependence has been observed in measurements of $\sigma_x(E)$ for the neutral systems and has been explained by invoking two separate mechanisms for projectile excitation.^{8,9}

IV. CONCLUSION

One of the most striking results of the present experiments is that, in the energy range investigated, values of $\sigma_e(E)$ for these alkali-metal anions are so different from those for H^- . Previous measurements²¹ of $\sigma_e(E)$ for H^- -rare-gas systems (H^- -X) indicate that thresholds for detachment are on the order of a few eV. Furthermore, values of the cross sections for H^- -X are at least 2 orders of magnitude greater (for energies below 50 eV) than the

present measurements for the corresponding Na^- , K^- -rare-gas systems (M^- -X). These low cross sections are presumably due to an ability of the M^- -X electronic wave function to adjust adiabatically during the collision. Thus, the electronic energy of M^- -X remains below that of M -X down to relatively small internuclear separations, as shown in Fig. 2. This adiabatic behavior may, in part, result from the fact that the collision times for M^- -X systems are five to six times longer than those for H^- -X.

Another source of the dissimilarities between M^- -X and H^- -X may involve correlation effects. It is well known²³ that H^- can be described by a split-shell ($1s\ 1s'$) configuration, implying that the correlation between the two electrons is primarily radial in character. On the other hand, recent calculations of the wave function of Na^- by Clark²⁴ indicate that angular correlation between the two outer electrons is dominant. Compared to the split-shell configuration, this angular correlation may allow more freedom for the electronic wave functions to adjust adiabatically and for the electrons to remain bound during a collision.

In this study two distinct mechanisms for electron detachment have been observed. The dominant process for detachment in the Na^- -Ne and K^- -Ar,Kr,Xe systems appears to involve a curve crossing, and it has been shown that the detachment probability near this crossing may approach unity. The other mechanism, which is responsible for the small cross sections discussed above, is operative at lower energies and is presumably due to a dynamical coupling between the molecular states. These mechanisms are similar to those proposed for neutral projectile excitation in the corresponding neutral systems.

Although present measurements of $\sigma_e(E)$ for Na^- -He appear to indicate a threshold for detachment, it is not clear whether the simple curve-crossing model which describes the Na^- -Ne and K^- -Ar,Kr,Xe systems can be invoked for this system. It is perhaps not surprising that a similar uncertainty exists in recent theoretical descriptions of the collisional dynamics of the neutral Na-He system.^{16,25}

ACKNOWLEDGMENTS

The authors wish to thank C. W. Clark for sending the results of his calculations for the Na^- wave function. We also thank J. B. Delos for several interesting conversations. This work was supported in part by the division of Chemical Sciences, Office of Basic Energy Sciences of the U. S. Department of Energy.

¹See, for example, R. L. Champion, *Adv. Electron. Electron Phys.* **58**, 143 (1982); A. Herzenberg and P. Ojha, *Phys. Rev. A* **20**, 1905 (1979); T. J. Morgan, *Comments At. Mol. Phys.* **12**, 319 (1983); J. S. Risley, *ibid.* **12**, 215 (1983).

²S. K. Lam, J. B. Delos, R. L. Champion, and L. D. Doverspike, *Phys. Rev. A* **9**, 1828 (1974); Y. Itoh, U. Hege, and F. Linder, *J. Phys. B* **16**, L167 (1983).

³J. P. Gauyacq, *J. Phys. B* **12**, L387 (1979); **13**, 4417 (1980); **13**, L501 (1980).

⁴R. D. Taylor and J. B. Delos, *Proc. R. Soc. London, Ser. A* **379**, 179; **379**, 209 (1982); T. S. Wang and J. B. Delos, *J. Chem. Phys.* **79**, 4306 (1983).

⁵W. M. Dukel'skii and E. Ya. Zandberg, *Zh. Eksp. Teor. Fiz.* **21**, 1270 (1951).

- ⁶Yu. F. Bydin, *Zh. Eksp. Teor. Fiz* **50**, 35 (1966) [*Sov. Phys.—JETP* **23**, 23 (1966)].
- ⁷N. Andersen, T. Andersen, L. Jepsen, and J. Macek, *J. Phys. B* **17**, 2281 (1984).
- ⁸V. Kempter, B. Kubler, and W. Mecklenbrauck, *J. Phys. B* **7**, 2375 (1974).
- ⁹W. Mecklenbrauck, J. Schön, E. Speller, and V. Kempter, *J. Phys. B* **10**, 3271 (1977).
- ¹⁰H. Alber, V. Kempter, and W. Mecklenbrauck, *J. Phys. B* **8**, 913 (1975).
- ¹¹J. Ø. Olsen, N. Andersen, and T. Andersen, *J. Phys. B* **10**, 1723 (1977).
- ¹²N. Andersen, T. Andersen, P. Hedegaard, and J. Ø. Olsen, *J. Phys. B* **12**, 3713 (1979).
- ¹³E. H. Pedersen, P. Wahnón, C. Gaussorgues, N. Andersen, T. Andersen, K. Bahr, M. Barat, C. L. Cocke, J. Ø. Olsen, J. Pommier, and V. Sidis, *J. Phys. B* **11**, L317 (1978).
- ¹⁴N. Andersen, T. Andersen, K. Bahr, C. L. Cocke, E. H. Pedersen, and J. Ø. Olsen, *J. Phys. B* **12**, 2529 (1979).
- ¹⁵C. Courbin-Gaussorgues, P. Wahnón, and M. Barat, *J. Phys. B* **12**, 3047 (1979).
- ¹⁶C. Courbin-Gaussorgues, V. Sidis, and J. Vaaben, *J. Phys. B* **16**, 2817 (1983).
- ¹⁷R. L. Champion and L. D. Doverspike, *Phys. Rev. A* **13**, 609 (1976).
- ¹⁸B. T. Smith, W. R. Edwards, L. D. Doverspike, and R. L. Champion, *Phys. Rev. A* **18**, 945 (1978).
- ¹⁹M. S. Huq, L. D. Doverspike, and R. L. Champion, *Phys. Rev. A* **27**, 785 (1983).
- ²⁰M. S. Huq, L. D. Doverspike, R. L. Champion, and V. A. Esaulov, *J. Phys. B* **15**, 951 (1982).
- ²¹R. L. Champion, L. D. Doverspike, and S. K. Lam, *Phys. Rev. A* **13**, 617 (1976); M. S. Huq, L. D. Doverspike, and R. L. Champion, *J. Phys. B* **15**, 951 (1982).
- ²²Data from W. Mecklenbrauck, Ph.D. thesis, Freiburg University, 1976, as shown in Ref. 12.
- ²³Recent theoretical work using this description of H^- is reported by V. Sidis, C. Kubach, and D. Fussen, *Phys. Rev. A* **27**, 2431 (1983).
- ²⁴C. W. Clark (private communication).
- ²⁵C. Courbin-Gaussorgues and V. Sidis, *J. Phys. B* **18**, 699 (1985).