Superthermal Component in an Effusive Beam of Metastable Krypton: Evidence of Kr_2^+ Dissociative Recombination

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(Received 13 April 1992)

A superthermal component in a metastable Kr* krypton beam produced in a Kr gas discharge has been observed and studied. Evidence is presented that this fast component is due to dissociative recombination of Kr_2^+, and that the excited Kr direct products of this reaction are predominantly in the $5s$ states. An effective method (time of flight) for studying the product states of dissociative recombination reactions is thus demonstrated.

PACS numbers: 34.50.Lf, 36.40.+d

The dissociative recombination (DR) of electrons in reactions of the type

$$e^- + AB^+ \rightarrow A + B + W \quad (1)$$

is the primary mechanism for the removal of electrons in low-pressure ionized gases containing molecular ions, such as the Earth's and planetary ionospheres and gas laser plasmas. The exothermicity may allow either or both of the products A or B to be electronically excited, even while being dissociated with a total center-of-mass (c.m.) kinetic energy W. The generally fast reaction rates of 10^{-6}–10^{-7} cm^3/s have been widely measured for many species, but very little is known about the electronic states of the product atoms, which often influence both the chemistry and the diagnostics of the system. The conventional methods of determining the product states, including measurements of the decay radiation, photoabsorption, and laser-induced fluorescence all suffer from various problems such as lack of sensitivity, background competition, and diffusion losses.

We report here a new determination of the reaction product states of Kr_2^+ DR by measurements of the c.m. kinetic energy release W, a technique that is not subject to the problems of previous studies and, as a result, can lead to different conclusions. This work is a by-product of scattering studies of metastable rare-gas atoms, using thermal metastable beams produced in electric discharges [1]. Previously, in preparation for such experiments, we had observed a superthermal component in an effusive beam of metastable argon produced in a gas discharge [2]. This superthermal component was first postulated to be due to the formation of Ar^{*-} and its subsequent acceleration toward the anode [2]. However, Peterson suggested that the fast Ar* resulted instead from the DR of the Ar_2^+ ion in the source discharge [2,3]. Currently we report the observation of a similar superthermal component in a metastable krypton beam, which we find results from Kr_2^+ DR. The results yield new information on the product states of the reaction [3], and this work demonstrates a very effective method of determining the final channels of DR reactions.

The apparatus used in this work is similar to the one used previously, but a few improvements have been made [4]. The source design has been modified to provide better accessibility and an improved slit arrangement gives greater accuracy in the determination of the chopper open time. In addition the flight path has been lengthened to 110.8 cm and a new pumping system maintains pressures about an order of magnitude lower. A schematic diagram is shown in Fig. 1.

Research grade krypton (Liquid Carbonics 0.9999) is supplied to the discharge by a flow controller coupled to a pressure monitor. The electron current in the discharge originates from a thoria coated tungsten ribbon (2.5 $\times$0.025 mm). The 0.13$\times$0.64 mm source exit slit forms a vertical ribbon beam which is collimated by a second set of slits 12.5 cm downstream to give a beam with an angular spread of about 1×10^{-3} rad. The slit size in the chopper wheel gives a chopper open time of 86 μs. The flight path passes through three separate vacuum chambers where the pressure is maintained at about 7×10^{-8} torr during an experimental run.

A set of sweep plates located between the exit slit of the discharge and the chopper maintain an electric field of about 250 V/cm across the beam path which removes all charged particles and long-lived Rydberg states. The beam enters the detector system through a 0.13-mm en-

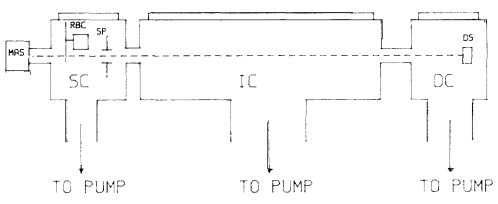

FIG. 1. The apparatus: metastable atom source (MAS); rotary beam chopper (RBC); sweep plates (SP); detector system (DS); source chamber (SC); interaction chamber (IC); detector chamber (DC).

trance slit and strikes a tungsten target plate; Auger electrons ejected from it are directed into a Channeltron electron multiplier. The length of the flight path ensures that all excited states except the metastables will decay before reaching the detector. The kinetic energy of the atoms is less than the work function of the target plate so that only metastable atoms or vuv photons can be detected. The photon peak (not shown here) appearing in the time-of-flight (TOF) spectrum is used to determine T_0, the time at which the chopper opens.

The data were collected with an Ortec multichannel scaler card and software operating in a Zenith personal computer. The channel width used in these experiments was 40 μs and the sweep length was 100 channels. The system delays were adjusted so that the T_0 channel was -2. The time between chopper open times is adjusted by varying the number of slits in the chopper wheel. In these experiments the beam pulse rate was 180 pulses/s, allowing sufficient time to observe the low velocity tail of the Maxwellian velocity distribution.

The effusive source is an efficient method of producing metastable atoms. At typical operating conditions in our apparatus, approximately 1.7×10^{8} metastable krypton atoms per s are emitted (into 2π sr), assuming 100% detection efficiency for our detector system, while a total of approximately 9.3×10^{15} krypton atoms per s (into 2π sr) are emitted giving a fraction of about 1.8×10^{-8} metastables per atom emitted.

The relative amount of the superthermal component in the metastable beam depends upon the source pressure, the electron current, and the discharge voltage, as discussed below. A typical set of data are shown in Fig. 2.

The data were fitted with the function

$$F(t)=(A_1/t)^4\exp[-2.5(A_2/t)^2] + A_3\exp[-(A_4-t)^2/0.36A_5]+A_6, \quad (2)$$

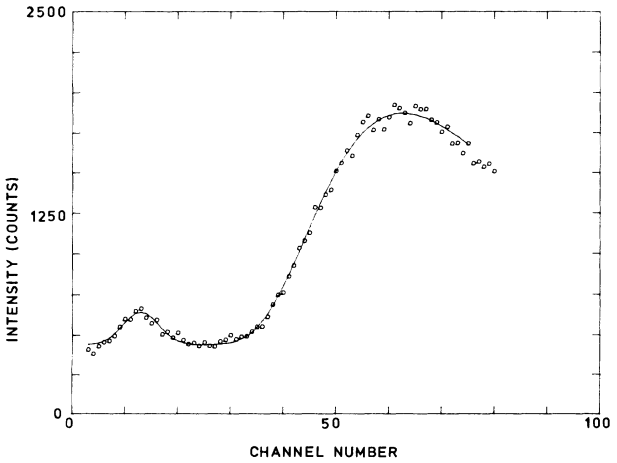

FIG. 2. Typical time-of-flight experimental data. The line shows the fit to the data with the function given in the text.

where the A's are the parameters determined by the fit and t is the time of flight. Parameter A_1 is the amplitude of the Maxwellian distribution while A_2 is its position. Parameters A_3, A_4, and A_5 are the amplitude, position, and width of the Gaussian distribution while parameter A_6 is the amplitude of the background. The first term represents the arrival time spectrum characterizing a Boltzmann thermal velocity distribution in a beam [5]. It accurately describes the onset of the main thermal distribution, including the broad peak. The slower part of the distribution in the tail beyond the peak is modified by losses from elastic and exchange scattering, whose cross sections increase with decreasing velocities. The scattering occurs primarily in the higher-pressure regions inside the source and just outside the anode slit. The second term represents a Gaussian velocity distribution for the superthermal component surrounding a single velocity $V_{\max}=L/t_{\max}$, where L is the length of the drift path between the chopper and the detector and $t_{\max}$ is the arrival time of the superthermal peak.

The least-squares fit was limited to channels from the fastest metastable atoms to those slightly past the peak of the Maxwellian distribution, in order to avoid the scattering losses mentioned above. A fit to the data is shown in Fig. 2.

It was found that the metastable yield is a linear function of discharge current over the 50–300 mA range used in the experiment. The experimental data were all normalized to the discharge current in each run. The area of the fast peak, determined from the Gaussian fit, as a function of discharge voltage and discharge pressure, is shown in Figs. 3(a) and 3(b). As can be seen in the plots, the discharge voltage used for the study of the metastable yield versus pressure was the voltage giving the maximum yield for the fast peak, and the pressure used for the study of the yield versus voltage was the pressure giving the maximum yield of the fast peak. Within the experimental error the amplitude of the Maxwellian distribution and the position of both the superthermal and Maxwellian peaks did not change. The velocity of the superthermal peak, V_0, was determined to be 1970 ± 130 m/s and the peak of the Maxwellian distribution occurred at 465 ± 1 m/s.

The data show that the metastable beam contains a superthermal component, in addition to a normal Boltzmann distribution. The superthermal peak can best be explained as resulting from DR of Kr_2^+ ions that were formed in the gas discharge. The first evidence that suggested DR as a likely cause of the fast peak in the Ar^* observed earlier [2] was that its arrival time seemed to be independent of all source parameters, while its size grew steadily with source gas pressure relative to the thermal peak. This behavior is consistent with the expectations for the formation of Ar_2^+ in the discharge, and the conclusion was justified by an analysis [3]. That analysis showed that the primary product states were $4s$ instead of

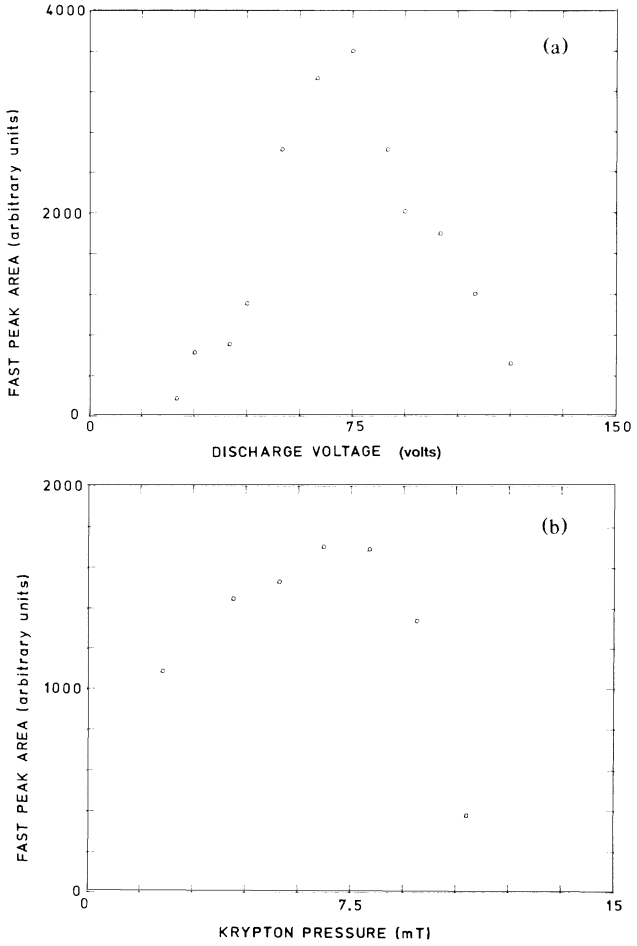

FIG. 3. (a) A plot of the area of the fast peak (arbitrary units) as a function of the discharge voltage. The error is about 10% in the determination of the area and in the measurement of the discharge voltage. These data were taken at a pressure P_{Kr} of 7.5 mT. (b) A plot of the area of the fast peak (arbitrary units) as a function of the krypton pressure P_{Kr} in the discharge. The errors are about 10% in area and 5% in pressure. These data were taken with a discharge voltage of 75 V.

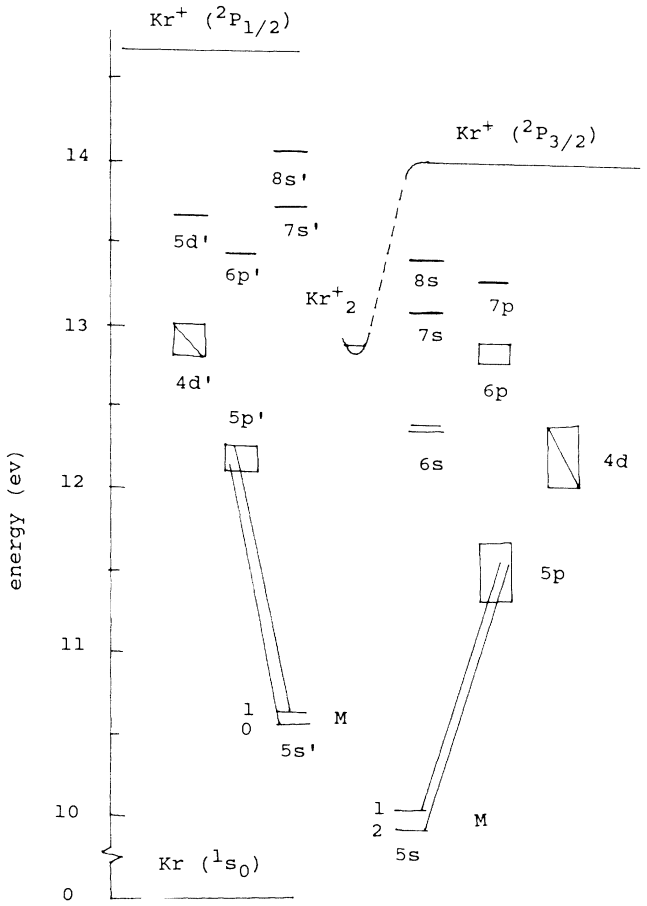

FIG. 4. Partial energy level diagram for krypton adapted from Shiu and Biondi [7] showing the major optical transitions they observed from the dissociative recombination of Kr_2^+. The $5s$ $J=0$ and $J=2$ levels are the metastable levels detected in this work; the $J=1$ levels radiate to the ground state.

$4p$ as previously believed [6]. Similar behavior with respect to the discharge parameters characterizes the fast peak in the Kr* beam reported here.

At pressures used in the metastable atom source [<10 mTorr; see Fig. 3(b)] the formation of Kr_2^+ by three-body association of Kr^+ is negligible, and molecular Kr_2^+ ions are formed primarily by associative ionization reactions

$$Kr^{**} + Kr \rightarrow Kr_2^+ + e \quad (3)$$

between a ground state Kr and a Rydberg state Kr** high enough in energy (above about 12.85 eV, the energy of the Kr_2^+ rovibrational ground state) for reaction (3) to be energetically possible at thermal energies. Figure 4 shows the energies of some of the states of Kr as well as that of Kr_2^+. The Kr** atoms are either excited from ground state Kr by the energetic primary electrons, or from metastable Kr* by the lower energy secondary electrons. The Kr_2^+ ions are rapidly neutralized by DR with slow electrons:

$$Kr_2^+ + e \rightarrow Kr_2^{**} \rightarrow Kr^* + Kr + W, \quad (4)$$

where the Kr_2^{**} is an unstable state that decays to Kr* + Kr, releasing W of kinetic energy to the two dissociative products. This dissociative decay of Kr_2^{**} is in competition with autoionization back to Kr_2^+. W, the total c.m. kinetic energy released, is equally divided between the atomic products, and is equal to the difference between the total initial energy (electronic, kinetic, and rovibrational) in $Kr_2^+ + e$, and the electronic energy in the Kr* product. The electronic energy of any Kr* produced in reaction (4) can be deduced by determining the corresponding value of W, which is obtained from the arrival time spectrum. Assuming a thermal distribution of Kr_2^+ in the ion source, which on the average has zero ve-

locity on the beam axis, the DR to a single Kr^* state will yield an approximate Gaussian velocity distribution in the laboratory, centered about $V_0=(W/m)^{1/2}$ where m is the Kr mass.

The Kr^* states from reaction (4) that correspond to the fast peak in our spectrum are the metastable $5s$ $J=2$ and 0. Any substantial contribution from $5p$ product states would also be observable because they all radiate rapidly to the $5s$ states that are detected here. That radiation constitutes most of the spectra from Kr_2^+ DR observed by Shiu and Biondi [7], indicated in Fig. 4. The $5s$ $J=1$ states produced either directly or by the decay of the $5p$ states do not contribute to our data, because they radiate directly to the ground state. The value of $V_0=1970\pm130$ m/s obtained from the data fit yields a W of about 3.35 eV. The statistically weighted W expected from the Kr^* $5s$, $J=2$ and $J=0$ states is 2.83 eV, for DR of rovibrationless Kr_2^+ and an electron energy of 0. The various $5p$ states from DR under the same conditions would yield much lower W values between 1.18 and 1.55 eV. The data suggest, then, that the $5s$ states predominate the direct products of Kr_2^+ in our apparatus and that the total rovibrational plus kinetic energy in the initial $Kr_2^+ + e$ system is about $3.35-2.83=0.52$ eV. The electrons can be expected to contribute about half of that energy and the rest must be mostly vibrational energy in the Kr_2^+. With this much energy one could expect some small variations in the arrival time of the fast spectrum, depending on the pressure (which reduces vibrational excitation) and the electron beam conditions, which can change the electron energy distribution. It is expected that whatever the energy distribution, the very low energy component will dominate the reaction, whose rate decreases with electron energy.

These results are evidently the first to find that the $5s$ states, instead of the $5p$ states, dominate the DR products as observed by Shiu and Biondi [7]. They do not contradict the experimental observations of Shiu and Biondi whose apparatus could not detect the vuv radiation from the $5s$ $J=1$ state. But even if that radiation were detected it would be difficult to quantify because of its resonant trapping in the ambient Kr gas.

These data demonstrate the usefulness of measurements of kinetic energy released to the dissociative products, for the determination of the DR product states. The fact that any radiation by the products does not affect W in Eq. (4) renders such determinations immune from any effects of cascading, and is a real strength of this technique of determining energy release spectra. The present technique is particularly useful for studying rare-gas species, whose metastable states are easily detectable (secondary electron emission from surfaces) at near thermal energies. It cannot detect the $5s$ and $5s'$ $J=1$ states that radiate to the ground state, but should detect all other states that are substantially populated among the initial products, because they cascade eventually to the $5s$ states.

We hope, in further studies using an extended flight path, to examine details of the shape and location of the fast peak at various pressures and electron beam conditions, in order to determine the small contributions from the $5p$ states.

J.R.P. was supported by NSF Grant No. PHY 9111872 and AFOSR Contract No. F49620-89-K-0002.

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