EXCITATION RESONANCES FOR THE PRODUCTION OF METASTABLE ATOMS IN LOW-ENERGY ARGON ION-ATOM COLLISIONS*

Paul O. Haugsjaa† and Robert C. Amme
Department of Physics, University of Denver, Denver, Colorado 80210

and

Nyle G. Utterback
AC Electronics, General Motors Corporation, Santa Barbara, California 93102
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Metastable argon atoms are found to be forward scattered along with ground-state atoms after $Ar^+ + Ar$ charge-transferring collisions. Using a detection technique involving Penning ionization of acetylene, it was found that the cross section for metastable excitation has a magnitude of the order of 10^{-3} Å^2 and exhibits two distinct low-energy resonances as a function of incident Ar^+ energy.

Knowledge regarding the formation of metastable atomic species during charge-transfer neutralization of ion beams is of considerable importance to workers in the field of atomic collisions, as is also the occurrence of excitation in the presumably adiabatic region.[1,2] We report here the first observation of twin energy resonances in the cross section for the production of metastable atoms scattered in the forward direction, formed during symmetric charge-transfer neutralization of argon beams. These resonances, whose peaks lie at 29- and 41-eV incident ion energy, have been observed through Penning ionization of acetylene by Ar*. The argon atom has two close-lying states which are metastable.[3] The first of these derives from the $(^2P_{3/2})$ 4s configuration with $J=2$, and the second from the $(^2P_{1/2})$ 4s configuration with $J=0$. These states lie at 11.55 and 11.72 eV, respectively, above the ground state.

The resonances were first observed during a study of argon-acetylene ionizing collisions involving neutral argon beams formed by charge transfer of argon ions in a cell containing argon. During $Ar^+ + Ar$ charge-transferring collisions, it is energetically possible to form forward-directed metastable argon atoms when incident ion energies are above 23.1 eV. Because argon metastables will Penning-ionize actylene molecules,[4] it is possible to detect the presence of metastable argon by observing the ionization which arises when the neutral argon beam passes through an acetylene target.

The method used to measure the ionization cross sections has been described previously.[5,6] Ground-state argon ions formed by electron impact in an ion source operated at about 10 mTorr with an ionizing-electron energy of 25 eV are extracted, electrostatically accelerated to the desired beam energy, and focused through a charge-transfer cell containing the neutralizing gas. Ions are removed, and the neutral beam thus formed is allowed to pass between parallel plates in a low-pressure target chamber where negative charge due to ionizing events is measured. The target chamber used in these measurements was isolated from the charge-transfer region by differentially pumped apertures. Since one may determine the neutral-beam intensity from ion-current measurements in the charge-transfer region,[5] the total ionization cross section can be established.

At neutral-argon-beam energies exceeding 29 eV, there is sufficient energy in the Ar-C_2H_2 c.m. system for direct ionization of C_2H_2 by a ground-state Ar atom. Therefore, in order to ascertain the contribution to the measured ionization by the metastable component, it is necessary to establish the ionization cross section for the ground-state case. One may obtain a neutral beam of entirely ground-state Ar atoms for this purpose by neutralization of a ground-state Ar^+ beam in H_2. Since the c.m. energy for $Ar^+ + H_2$ collisions is only 1/21 of the incident ion energy, no metastable Ar neutrals can be formed below a beam energy of 242 eV.

Figure 1 shows the results of measurements of the ionization cross sections for Ar-C_2H_2 collisions using both argon and hydrogen as neutralizing gases. For the argon-neutralized case, one has a beam which contains some excited atoms, but for the H_2-neutralized case the beam atoms are all in the ground state. One notes that for the argon-neutralized beam the cross section rises abruptly below an incident ion energy of 10 eV, in the argon-acetylene c.m. system,

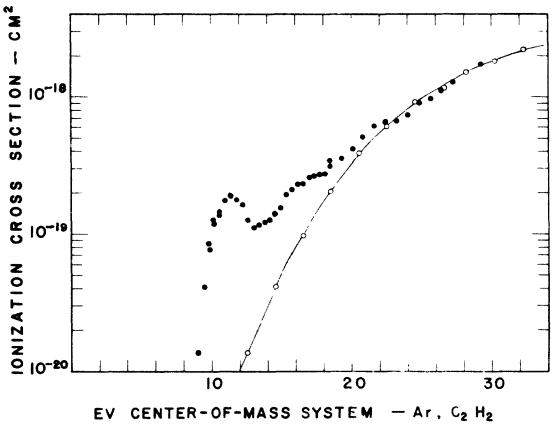

FIG. 1. Ionization cross sections for argon-acetylene collisions. Open circles: 100% ground-state argon-atom beam formed by neutralization of Ar^+ in H_2. Closed circles: mixed-state argon-atom beam formed by neutralization in Ar.

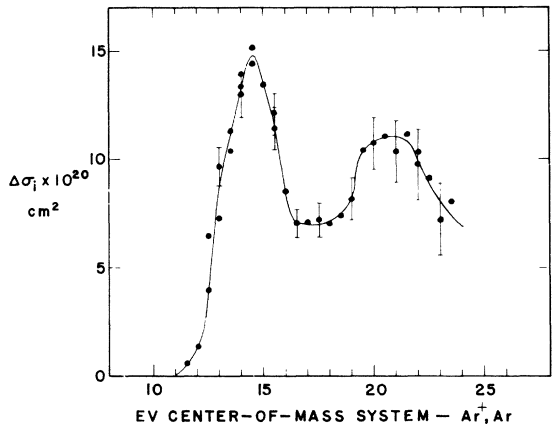

FIG. 2. Difference between cross sections in Fig. 1 expressed as a function of energy in the Ar^++Ar c.m. system. Ordinate is a measure of the percentage of metastables in the beam formed by symmetric charge transfer.

which is below the ionization potential for acetylene, 11.4 eV, and therefore must be the result of excitation in the neutral beam. However, the cross section for the hydrogen-neutralized beam is well behaved, rising smoothly from just above threshold for the ionization process to join the argon-neutralized-beam measurements above 22 eV in the c.m. system. The difference between the two measurements must be due to long-lived excited atoms in the neutral argon beam produced by

$$Ar^+ + Ar \rightarrow Ar^* + Ar^+ . \quad (1)$$

The excited atoms give rise to Penning ionization in the C_2H_2 target and raise the measured cross section.

The difference between the two cross sections is shown in Fig. 2 as a function of the energy available in the Ar^+-Ar c.m. system. The error bars shown on the figure are representative of upper limits to the random errors involved in the measurement. They were found by carrying through the calculation for the difference in the cross sections an 8% random instrumental uncertainty in the measurement of the beam intensity and ionization current for the argon-neutralized case. It is evident that at least two resonances appear in the difference cross section, indicating the formation of long-lived excited states in the neutral argon beam by process (1), with maxima occurring at 14.6 and 20.5 eV in the argon-ion–argon c.m. system.

The difference in the two cross sections at any particular incident beam energy is a measure of the ratio of metastable- to ground-state atoms in the beam, B_m/B_g. It is possible to make an approximate calculation of the magnitude of this ratio on the basis of data presently available. If one assumes that all deexcitation of the metastable component of the beam gives rise to ionization with cross section σ_P and that the number of metastables in the beam is small compared with the number of ground-state atoms (an assumption well justified by the result), one may write $B_m/B_g = (\sigma_{Ar} - \sigma_H)/\sigma_P$. Here σ_{Ar} and σ_H are the observed ionization cross sections for argon-acetylene collisions with the beam neutralized in argon and hydrogen, respectively. Thus, if one knows the Penning ionization cross section σ_P for the metastable states and energies concerned, it is possible to determine the ratio B_m/B_g. Linear extrapolation of measurements of the deactivation cross section for argon metastables in acetylene reported by Hollstein et al.[4] between 70- and 500-eV incident Ar* energy yields a value of about 60 Å² at 6 eV, which is about the energy that forward-scattered metastables would have if formed below the peak of the first observed resonance. Assuming that this cross section is very nearly σ_P, one has $B_m/B_g \approx 2.5 \times 10^{-5}$. This ratio is, of course, equal to the ratio of the cross section for metastable excitation during charge transfer to the cross section for symmetric resonant charge transfer. Since the latter is known[7] ($\sigma_q = 40$ Å² at 29 eV), it is estimated that the cross section for metastable excitation during symmetric charge transfer is $\sigma_m \approx 10^{-3}$ Å² at 29-eV incident Ar^+ energy. All metastables observed were those scattered within a forward cone with 4° half-angle.

In order to set closer limits on the energy of the state or states involved, measurements were also made of the ionization cross section for methane by argon beams neutralized in both argon and hydrogen. Since methane has an ionization potential of 13.0 eV, the excitation of any long-lived excited states above 13 eV can be detected through ionization measurements as above, provided that the Penning cross sections are comparable. No difference between the ionization cross sections for the two charge-transfer gases was observed, suggesting that the long-lived excited states involved have excitation energy between 11.4 and 13.0 eV. It is concluded that the two resonance peaks we have observed in the excitation cross section are only due to atoms in the two low lying metastable states of argon at 11.55 and 11.62 eV.

The existence of two peaks could be explained if a higher lying electronic state is excited at a beam energy of ~40 eV which subsequently decays to one of the two metastable states. Alternatively, they could be separate resonances for the direct excitation of these two close-lying states.

One of us (N.G.U.)[2] has previously observed a resonance in the excitation of metastable states in slow helium ion-atom collisions. However, in this case, only a single resonance peak could be observed.

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A PULSED ELECTRON-NUCLEAR DOUBLE-RESONANCE EFFECT*

I. M. Brown, D. J. Sloop, and D. P. Ames
Research Division, McDonnell Douglas Corporation, St. Louis, Missouri 63166
(Received 10 January 1969)

Pulsed electron-nuclear double-resonance effects in phosphorus-doped silicon were studied by monitoring the electron spin echo arising from the donor electron. The application of a four-pulse sequence of EPR and NMR pulses was found to produce a periodic attenuation and restoration of the electron spin echo as the carrier frequency of the rf pulses was swept. This phenomenon is explained by considering the z component of the local field produced at the donor electron by surrounding shells of distant Si^{29} nuclei.

Several years ago Feher[1] reported a comprehensive investigation of electron-nuclear double-resonance (ENDOR) experiments in n-type silicon. This present Letter describes pulsed ENDOR measurements which we have performed on phosphorus-doped silicon. In our studies the electron spin echo was monitored for ENDOR. Although Mims[2] has described the observation of pulsed ENDOR by changes in the height of the stimulated electron spin-echo signal, the investigations reported here involve a new phenomenon which results from the use of novel pulse sequences. We have found it advantageous to work with phosphorus-doped silicon since the electron T_2 is relatively long,[3] thereby allowing sufficient time for applying several rf pulses at various times relative to the microwave pulses. The new effect reported here resulted from the application of a four-pulse sequence of alternating microwave (EPR) and radio frequency (NMR) pulses shown in Fig. 1(b).

A superheterodyne X-band spectrometer with pulsed capabilities was employed and the static magnetic field was fixed at one of the two phosphorus hyperfine EPR lines. Microwave pulse widths of 150 nsec and peak powers of about 100 mW were required to achieve a nutation angle of 90°. In our samples the phosphorus concentration was sufficiently low ($\approx 3\times 10^{16}$ atoms/cc) so that the electron spin-lattice relaxation time at