Negative-Ion Formation in Rydberg-Atom Interactions ($n = 7$–40)

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We describe the first experiments in which negative ions formed in interactions involving highly excited (laser-selected) atoms are identified by mass. We therefore report the first observations of negative ions produced by Rydberg–ground-state interactions (at low n) and by Rydberg-Rydberg interactions (at high n).

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The study of positive-ion formation in resonantly excited vapor dates back to 1926 when Mohler, Foote, and Chenault[1] observed peaks in the "photosensitivity" of cesium vapor upon illumination by light at principal-series wavelengths. Subsequent experiments[2] were directed toward identification of the ion-formation mechanisms with primary emphasis on associative ionization,

$$A^* + A \rightarrow A_2^+ + e, \quad (1)$$

where the asterisk represents electronic excitation. In 1965 Lee and Mahan[2] suggested that ion-pair formation,

$$A^* + A \rightarrow A^+ + A^-, \quad (2)$$

could also lead to ions and later experiments[3,4] supported this. In 1984 Cheret and Barbier[5] reported direct observation of Rb^- from Rb($5s$)-Rb($6d$) collisions.

Here we report results of the first experiments in which negative ions formed in interactions involving Rydberg atoms ($n = 7$–40) are identified by mass. Using laser-excited sodium atoms we find that reaction (2) dominates at low n, but, surprisingly, ion-pair formation involving two Rydberg atoms dominates at high n. This is the first time that energy-pooling reactions leading to negative-ion formation have been observed. Because these energy-pooling cross sections are quite high, about one-tenth geometric, the results should be of interest to workers in a variety of fields, including solar physics, astrophysics, and plasma physics, as well as those engaged in studies of the intrinsic properties of atoms.

The observation that Na^- is formed in processes in-

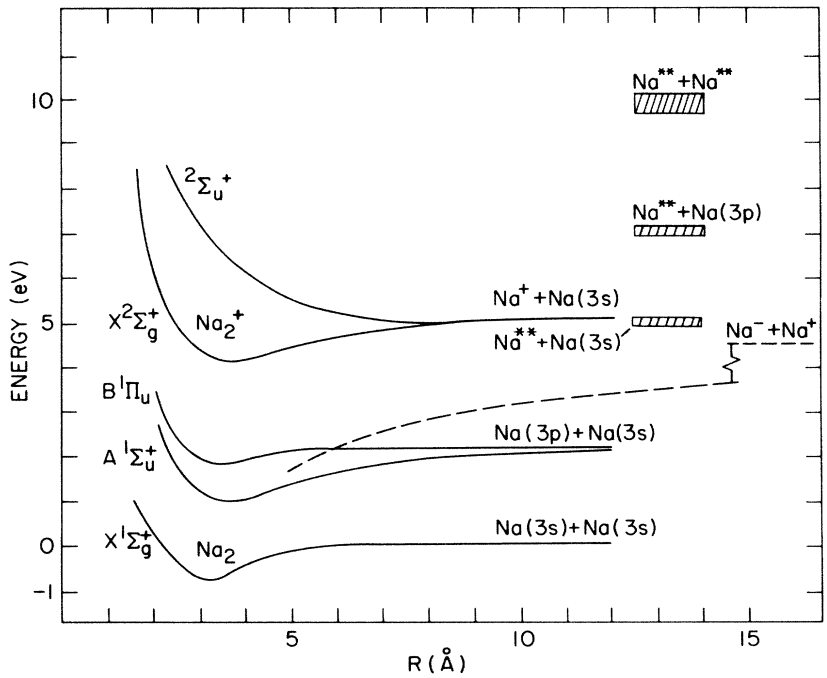

FIG. 1. Partial energy-level diagram for Na and Na_2. The cross-hatched regions represent Na($n = 7$–40), the range of principal quantum numbers for these experiments.

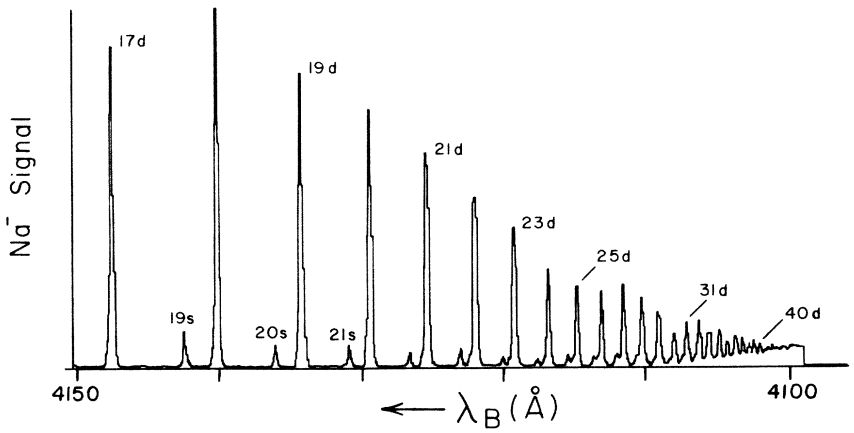

FIG. 2. Na^- signal as a function of λ_B.

volving two Rydberg atoms is surprising because, as illustrated in Fig. 1, the reaction

$$Na^{**} + Na^{**} \rightarrow Na^+ + Na^-, \quad (3)$$

where Na^{**} is a *highly* excited atom, is exothermic by ~ 5.5 eV if the products are in their respective ground states. Since $(Na^+)^*$ is energetically precluded and stable excited states of Na^- have not been observed, energy disposal in excess of 5 eV is probably required.

Excited sodium atoms were produced by two-step (pulsed) laser excitation, $3s \rightarrow 3p \rightarrow nl$, where l is either s or d. However, angular momentum mixing rapidly leads to a statistical distribution of l states[6] (at high n). Ions were electrostatically extracted from the reaction region containing sodium vapor at $\sim 10^{11}$–10^{12} cm^{-3}, mass analyzed, and detected. In order to make the collection efficiency, κ, for positive and negative ions nearly equal, the magnitude of the multiplier cathode potential was always 1 kV and the overall voltage 3 kV. Both Na^+ and Na_2^+ were observed[6,7]; however, the only negative ion formed was Na^-.

Figure 2 shows the Na^- signal versus λ_B, the wavelength of the blue ($3p \rightarrow nl$) laser, with λ_Y, the setting of the yellow ($3s \rightarrow 3p$) laser, fixed at the D_2 wavelength. Since the spectral power of the blue laser varied by less than 10% over the range shown, the decrease with increasing n is a true indication of the relative efficiency of production of Na^-.

Formation mechanics were investigated by study of the dependence of the Na^- signal on yellow- and blue-laser power densities and sodium-atom density, N. All N dependences were quadratic, indicating that two sodium atoms are required to form a single Na^-.

Figure 3 shows the Na^- signal versus blue-laser power density at two values of n, 20 and 7. It is clear that Na^- formation at the low n requires only one blue photon, but two are necessary at $n = 20$. At intermediate n the slope is between 1 and 2, indicating contributions from both linear and quadratic processes. Although the range of yellow power densities over which the Na^- signal varied was limited by saturation of the $3s \rightarrow 3p$ transition, a quadratic dependence was observed for high n. These observations show that two Rydberg atoms are required to produce Na^- at high n, and, together with the conclusion drawn from N-dependence data, eliminate three-body processes as

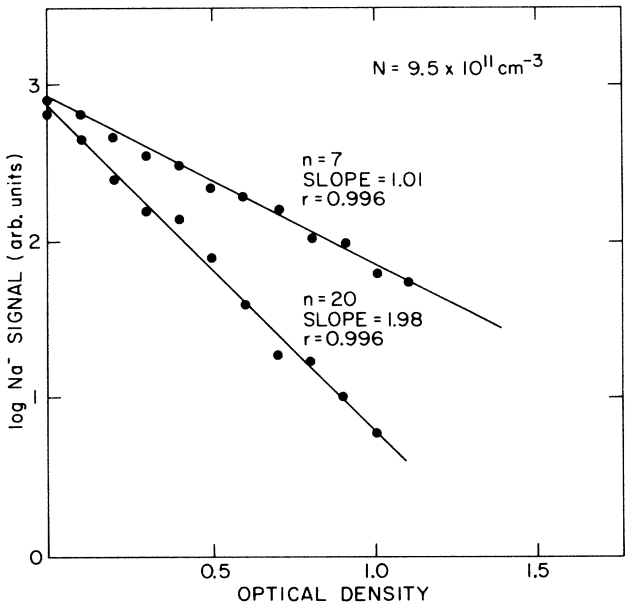

FIG. 3. Na^- signal as a function of blue-laser power density for the indicated principal quantum numbers; both are associated with laser excitation to the d state. The optical density is the logarithm of the laser-beam attenuation by a neutral density filter so that the graph is a log-log plot. The straight lines are least-squares fits to the data with correlation coefficient r. Each data point was acquired with 100 laser pulses.

a possible source of Na^-. The linear blue dependence at low n strongly suggests that reaction (2), with $A = Na$, is dominant. This reaction is exothermic for all states considered in this study (see Fig. 1).

While the high-n data show that two Rydberg atoms lead to a single Na^-, it is not necessary that Na^- be formed *directly* in Na^{**}-Na^{**} collisions. It is possible that a free electron from a blackbody-photoionized Na^{**} attaches to a second Rydberg atom. Such a process would also require disposal of ~ 5.5 eV, in this case as radiation, to stabilize Na^- in the ground state. Although this is possible, in the remainder of this paper we assume that Na^{**}-Na^{**} collisions directly lead to Na^- at high n.

We may estimate the rate constant at high n, k^-, by measuring the number of Na^- produced per laser pulse, Q^-, which is approximately

$$Q^- = \kappa[N_0^{**}]^2 V[\tau/2]k^-, \quad (4)$$

where V is the reaction volume, τ the effective lifetime of Na^{**}, and N_0^{**} the initial concentration of Rydberg atoms. The treatment of Ref. 6 may be used to include the spatial dependence due to diffusion, but, as discussed in that report, the approximations used to obtain Eq. (4) are adequate for the evaluation of heavy-body reaction rates in these experiments.

A similar expression for Q^+, the number of Na_2^+ from reaction (1), with $A^* = Na^{**}$, may be written.[6] Dividing, we obtain

$$Q^-/Q^+ = \tfrac{1}{2}[N_0^{**}/N][k^-/k^+], \quad (5)$$

where k^+ is the rate constant for associated ionization. Equation (5), together with our data and our previous measurement[6] of k^+, leads to an estimate of $k^- \approx 10^{-7}$ cm^3 sec, corresponding to a cross section $\sigma^- \approx 10^4$ Å^2, at $n = 20$. This value, while huge compared to cross sections for processes involving "ordinary" atoms, is about 10 times *lower* than the self-l-mixing cross section.[6] Thus, negative-ion formation occurs with l-mixed reactant Rydberg atoms, and the measured σ^- is associated with an appropriate average over l.

We checked the magnitude of σ^- by measuring the negative-ion signal immediately outside the reaction cell using time of flight to separate it from the electron signal. This yielded a value within a factor of 4 of that reported above. This relatively high cross section suggests the use of Rydberg-Rydberg interactions to generate the intense negative-ion beams required for neutral beam heating of a plasma.[8]

In our experiments on positive-ion formation[7] we observed Na^+ from Na^{**}-Na^{**} collisions. The cross section was found to be gigantic, about ten times geometric, consistent with the theoretical prediction of Olson.[9] Olson also predicted that ion-pair formation is a *relatively* important source of Na^+ at thermal energies, consistent with our measured ion-pair cross section (about one-tenth geometric). Further, if Olson's high-velocity cross sections for negative-ion formation in Rydberg-Rydberg collisions are extrapolated to thermal energies, the result, $\sim 4\times 10^3$ Å^2, is also consistent with our estimates.

The method of estimating σ^- at high n cannot be applied at low n because the associated ionization cross sections are unknown. However, a crude estimate based on the magnitude of the signals suggests that it is much lower, ~ 10 Å^2, which is of ordinary magnitude, as is the value reported by Cheret and Barbier[5] for Rb($6d$)-Rb($5s$) ion-pair formation.

The precise method of energy disposal for the highly exothermic Rydberg-Rydberg process is uncertain. The simplest (and least exotic) method is sharing of the ~ 5.5 eV as kinetic energy of the Na^+ and Na^- products. This requires the $Na^{**} + Na^{**}$ system to evolve from the entrance channel, at ~ 10 eV in Fig. 1, to the $Na^+ + Na^-$ exit channel via a series of crossings with (unknown) potential energy curves in the ~ 5–10-eV range. These curves are not indicated in Fig. 1, but clearly many exist.

Another possibility involves formation of doubly excited Na^- with outer electrons in correlated Rydberg orbits. While this would provide an exit channel that is close to the entrance channel, such a state of this "planetary negative ion," which would be imbedded in the $Na + e$ continuum, would have to have an autodetachment lifetime in excess of ~ 1 μsec to be observed in our apparatus. Therefore, while this is a possibility it must be regarded as highly speculative.

A third possible method of energy disposal is radiative ion-pair formation,

$$Na^{**} + Na^{**} \rightarrow Na^+ + Na^- + \hbar\omega \ (\sim 5.5 \text{ eV}). \quad (6)$$

Because of the long-range nature of the Coulomb force, photon energies in excess of 5.5 eV can also occur. Within the context of the free-electron model[11] of Rydberg-atom interactions in which collisions with a second heavy body, in this case another Rydberg atom, are treated as collisions with the Rydberg electron, such a process would be similar to radiative attachment and lead to an "affinity spectrum."[12] The free-electron model has been shown to be valid for electron transfer, from xenon Rydberg atoms to a variety of ground-state polyatomic molecules.[13] Furthermore, the solar spectrum is known to be strongly influenced by radiative attachment of free electrons to H atoms in the photosphere.[14] The inverse process, photodetachment accompanied by neutral excitation, has been observed in the laboratory.[15] To investigate this interesting possibility we searched for 5.5-eV photons using a 2250-Å filter with 100-Å bandwidth and 4 optical density rejection. Although a small signal was detected, we cannot discount the possibility that it was

fluorescence from the principal series (limit ~ 2400 Å). On the basis of the observed Na^- signal, detector sensitivities, and apparatus geometry, we estimate that the maximum number of photons that we would observe is only ~ 50 per laser pulse. Therefore, replacing the filter with a monochromator gave no signal at ~ 2250 Å, but we did observe principal-series emissions, leading to our caution in attributing the signal observed with the filter to radiation from reaction (6). While our attempts to detect these photons are equivocal at this time we believe that this interesting possibility should be pursued.

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