Electron Scattering Resonances in Fast D(High n)-N_2 Collisions

Peter M. Koch
J. W. Gibbs Laboratory, Yale University, New Haven, Connecticut, 06520
(Received 4 June 1979)

The results of the first measurements of the velocity dependence of the total ionization σ_I and the total destruction σ_d (ionization + excitation + deexcitation) cross sections for fast Rydberg-atom-neutral-molecule collisions are presented. The observed resonant structure in and the absolute magnitudes of σ_I and σ_d unambiguously confirm the prediction that the Rydberg electron bound to a fast atom scatters quasifreely. The data also strongly hint that the ionic core does the same.

How Rydberg atoms $R(n)$ with principal quantum number $n \gg 1$ are affected by collisions with neutral and charged particles Y has recently been an active theoretical[1] and experimental[2] research topic. One useful parameter that is especially important for characterizing the results presented in this Letter is the ratio v_T/v_0 of the relative velocity v_T of $R(n)$ and Y to the orbital velocity v_0 of the Rydberg electron e_R^-.[3] Experiments with $R(n)$ and neutral targets Y in thermal beams and in vapor cells have all investigated the "slow" collision regime, $v_T/v_0 \ll 1$, in which the translational momentum of the incident e_R^- is small compared to its atomic orbital momentum. The recent theoretical work in this regime of Matsuzawa and other workers is built on the foundation laid by Fermi.[3]

In the opposite limit, $v_T/v_0 \gg 1$, Butler and May[4] first predicted that the cross section σ_I for ionization of the e_R^- in H(high n) + H(1s) collisions at velocity v_T should be approximately equal to the total scattering cross section σ_e for free electrons colliding with H(1s) at the same relative velocity $v_e = v_T$. The physical basis for this prediction, subsequently generalized by Smirnov,[5] is simple: Processes which change the momentum p_0 of the e_R^- by an amount $\Delta p \gg p_0$ will lead to ionization. For the present velocity range, σ_e is dominated by such changes, so that $\sigma_I \simeq \sigma_e$. This also leads to the prediction that σ_I should be *independent* of n when $v_T/v_0 \gg 1$. This is not the case when $v_T/v_0 \ll 1$.

This Letter reports the first experimental confirmation of both these predictions in two related D(high n)-N_2 collision experiments.[6] The collision partners were deliberately chosen for three reasons. First, for $1.5 \lesssim E_e \lesssim 3.5$ eV free e^--N_2 scattering has a large σ_e dominated by a series of $N_2^-(^2\Pi_g)$ compound-state–induced resonances. This process has been studied extensively,[7,8] both experimentally and theoretically. Second, 6–13-keV D(high n) atoms have velocities v_T that span the resonance region of σ_e. Third, techniques for producing in this energy range H(high n) atoms in "n bands"[9] and in Stark-tuned, laser-pumped, individual quantum levels[10] have been demonstrated previously.

The first experiment used the apparatus shown schematically in Fig. 1(a) to measure σ_I for process I, $D\{35 \lesssim n \lesssim 50\} + N_2 \rightarrow D^+ + e^- + N_2(\Sigma)$, where

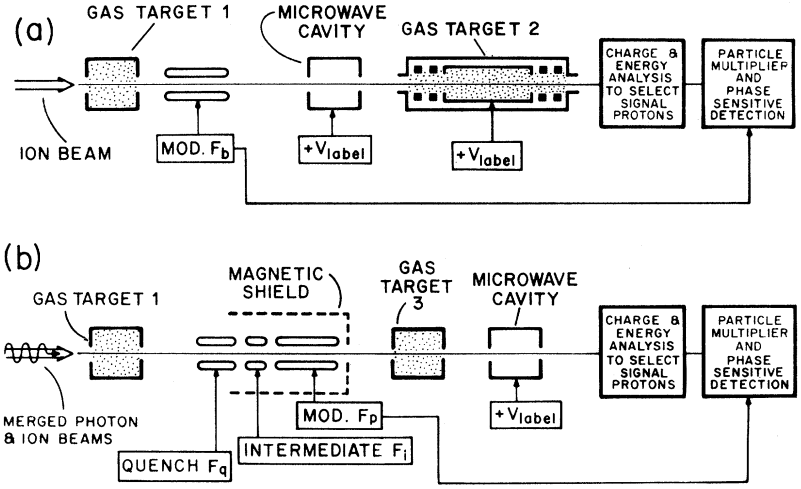

FIG. 1. Important features of the apparatus used to measure (a) σ_I, and (b) σ_d for D(high n)-N_2 collisions.

Σ refers to all possible final states of N_2. A cw beam of $D(n)$ atoms with excited states weighted by n^{-3} was produced by D^+-C_8F_{16} electron transfer collisions in gas target 1. Experimental signals produced by the n band $\{n\}=\{35\lesssim n\lesssim 50\}$ were defined with use of field ionization by passing the $D(n)$ beam through a static electric field F_b, square-wave modulated at 1 kHz between 110 and 420 V/cm. The energy-labeling technique[9] and lockin detection were used to measure the intensity of various D^+ signals produced by ionization of $D\{n\}$ atoms inside one or the other of two devices which could be voltage labeled ($V_{\text{label}}=100$ V), the microwave cavity or gas target 2.

When V_{label} was applied to gas target 2, an energy-labeled D^+ signal was produced not only by the desired process I (scattered beam intensity I_+'), but also by $D(2s)+N_2\rightarrow D^+ + e^- + N_2(\Sigma)$ collisions, since the $D(2s)$ atoms in the beam underwent modulated Bethe-Lamb quenching[11] in F_b. These $D(2s)$ atoms were quenched, however, (survival $<10^{-5}$) by driving resonantly the $2s_{1/2}$-$2p_{3/2}$ transition in the TM_{020}-mode cavity ($\omega/2\pi=9.91$ GHz) with an empirically set low-power level P_{low} which quenched $<3\%$ of the $D\{n\}$ flux. An empirically set P_{high} was used to quench the entire $D\{n\}$ flux by microwave multiphoton ionization.[12] Thus, difference signals ($P_{\text{high}}-P_{\text{low}}$) were produced only by atoms in $\{n\}$.

When V_{label} was applied to the cavity instead, the ($P_{\text{high}}-P_{\text{low}}$) energy-labeled D^+ multiphoton ionization signal yielded the intensity $I\{n\}$ of atoms in $\{n\}$. It was typically 6 ppm of the total neutral-beam intensity $I_0\sim 3\times10^{11}$ sec^{-1}, which was measured with an electrometer as a secondary-electron–emission current in a Faraday cup.

In order to subtract background gas contributions to signals, $P_{\text{high}}-P_{\text{low}}$ measurements of I_+', $I\{n\}$, and I_0 were made both with N_2 directed into gas target 2 (gas "in") and with the same N_2 flow directed into the surrounding vacuum chamber (gas "bypass").[13] They were repeated $\gtrsim 30$ times and averaged for each E_D. To keep the target density constant, the pressure difference for N_2 gas in minus gas out was monitored with an ion gauge.

The present results for σ_I are shown in Fig. 2 as open circles, for $v_T/v_0\gtrsim 25$. The scatter is a measure of the reproducibility of the data. Since $I_0/I\{n\}>10^5$, a large, unmodulated, energy-labeled D^+ flux produced by $D(1s)$-N_2 collisions contributed noise which severely degraded the I_+' measurements. In Fig. 2, σ_e (Refs. 7 and 8)

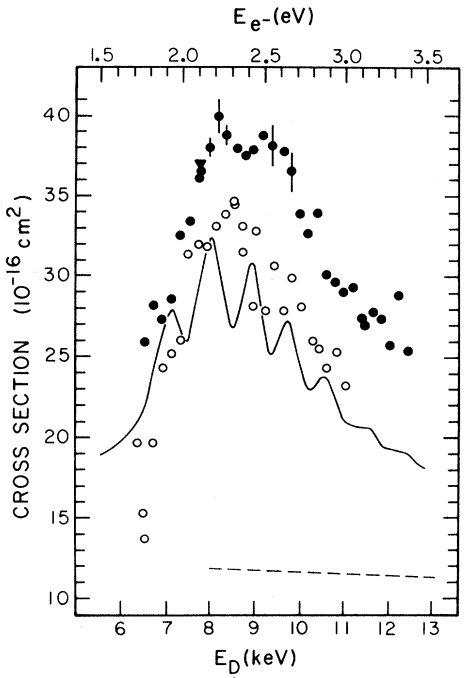

FIG. 2. Present results: open circles, σ_I; closed circles, $\sigma_d(n^*=46)$; inverted triangle, $\sigma_d(n^*=71)$. The absolute scale (with suppressed zero) was established with estimated error $<20\%$ by normalization to σ_{10} at 8 keV. Solid line, experimental curve for σ_e (Ref. 7). Dashed line, experimental curve for σ_{10} for H^+-N_2 collisions (Ref. 13), plotted vs $E_{D^+}=2E_{H^+}$.

is shown as a solid line with its energy scale placed so that $v_e=v_T$. The agreement between σ_I and σ_e, both in overall shape and in absolute magnitude, is rather striking, although σ_I appears to fall off more rapidly than σ_e on the low-energy side of the gross peak. The quality of the data obscures possible vibrational substructure in σ_I. These results are the first experimental confirmation of the approximate equality of σ_I and σ_e in the limit $v_T/v_0\gg 1$.

Small-angle scattering of the essentially unscreened nucleus of the D(high n) atom by the polarization interaction with N_2 can also contribute to σ_I. A formula derived by Smirnov[5] leads to an estimate of $\sim 0.8\times10^{-16}$ cm^2 for this process, which is negligible on the present scale.

To measure σ_d for D(high n)-N_2 collisions, a second experiment (II) was performed with use of the modified apparatus shown in Fig. 1(b). D^+-Xe electron transfer collisions prepared an n^{-3} weighted $D(n)$ beam as before, but a constant $F_q=30$ kV/cm ionized all atoms with $n\gtrsim 12$ (Ref. 10) and completely quenched all $D(2s)$ atoms.[11] A cw, collinear, ~ 20-W/cm^2 photon beam from a frequency-stabilized[14] $^{12}C^{16}O_2$ laser [9-μm, $P(18)$

or $P(20)$ line] drove $n=10$ to $n^*=46$ transitions to prepare a fast $D(n^*)$ beam with intensity $I(n^*) \sim 10^5$ sec^{-1}. To Stark tune the transition off and on resonance, the electric field F_p was square-wave modulated between zero and a few V/cm (reset for each E_D because of the v_T dependence of the Doppler shift).[12] Phase-sensitive detection at the 27-Hz modulation frequency isolated the $D(n^*)$ signal. Notice that this Stark-switching technique produced with fixed-frequency laser radiation a pure $D(n^*)$ beam with a continuously variable v_T.[15]

As in process I, microwave multiphoton ionization[12] of the $D(n^*)$ atoms inside a voltage-labeled cavity ($V_{label}=250$ V, TM_{010} mode, $\omega/2\pi=9.91$ GHz was used to measure $I(n^*)$. When N_2 was fed to gas target 3, this signal was reduced by collisional destruction of the $D(n^*)$ atoms. Notice that in this *transmission experiment*, neither D(2s)- nor large D(1s)-produced ion signals were generated, which is a distinct advantage. A digital time signal and digitized analog signals proportional to $I(n^*)$ and to I_0 were processed by an Intel-8080-microprocessor–based data collection system.

The measured σ_d values for the process $D(n^*=46)+N_2 \rightarrow D(n \lesssim 28$ and $n \gtrsim 61)+N_2(\Sigma)$ are shown in Fig. 2 as closed circles. The n limits for the final state were determined to contribute to the signal as follows. Atoms with $n \gtrsim 61$ (*including continuum states* $D^+ + e^-$) were ionized either directly in the collision or in the fringe field $F_f \simeq 46$ V/cm created before the cavity by V_{label}. Atoms with $n \lesssim 28$ were observed not to be ionized by the microwave field strength used for the experiment. Even though the σ_d curve lies 6–10 Å^2 above the σ_e curve over most of its range, it is immediately clear that they have similar v_T dependences. This is an unambiguous confirmation of the quasifree scattering of the e_R^-. The 6.4 meV binding energy of $D(n^*)$, however, may cause the N_2^--induced resonant structure[7,8] to be shifted toward slightly higher v_T. As was seen for σ_I, σ_d appears to drop off more rapidly than σ_e below ~7.5 keV.

Also shown in Fig. 2 is one point taken with a $D(n^*=71)$ beam prepared by 9-μm, $R(20)$ laser excitation of $D(n=10)$. To avoid ionization of $D(n^*)$ in F_f, V_{label} was reduced to 80 V. Within experimental error $\sigma_d(n^*=71)=\sigma_d(n^*=46)$, which confirms the predicted n independence of the cross section, at least for this one point. Notice that σ_d is ~10^6 smaller than the geometrical value $n^4\pi a_0^2 \simeq 2\times10^{-9}$ cm^2 for $n^*=71$.

A plausible explanation for the approximately constant upward displacement of σ_d relative to σ_I and σ_e is quasifree scattering of the D^+ nucleus of the $D(n)$ atom. The most likely D^+-N_2 scattering event in the present energy range is electron transfer, $D^+N_2 \rightarrow D(\Sigma n)+N_2^+$, where Σn is predominantly 1s. The measured cross section[13] σ_{10} for this process is shown as a dashed line in Fig. 2. Notice that it is nearly constant as a function of E_D and that over most of the present energy range $\sigma_e+\sigma_{10} \simeq \sigma_d$.

We thus have an especially simple view of these fast collisions: When the e_R^- gets close to a target atom or molecule, it scatters quasifreely while the nucleus acts as a distant spectator. When the nucleus gets close to a target, the opposite happens. Since the radius of the $D(n^*=46)$ atom is $n^2a_0 \sim 1100$ Å, this is not too surprising. In the $D(n^*)$-N_2 system, destruction proceeds predominantly via autodetaching negative-ion states: $N_2^-(^2\Pi_g)$ when the e_R^- scatters quasifreely and $D^-(1s, n \simeq n^*)$ when electron transfer to the D^+ nucleus takes place. In each case the probability is very low for the detached electron to reattach itself to a positively charged object, and so it escapes.

An estimate of the effective energy resolution in e_R^- scattering experiments is straightforward. The maximum (+) and minimum (–) kinetic energies of the e_R^- are $E_\pm=\frac{1}{2}m(v_T \pm v_0)^2$. $\Delta E/\overline{E}=4v_0/v_T$, where $\Delta E=E_+-E_-$ and $\overline{E}=(E_++E_-)/2$. Notice that $\Delta E/\overline{E}$ decreases with increasing $\overline{E}$. For a microcanonical distribution[1] of orbital momenta, $v_0=(\sqrt{3}n)^{-1}$ a.u. is the most probable orbital velocity. For experiment II, $28 \lesssim v_T/v_0 \lesssim 40$, $0.10 \lesssim \Delta E/\overline{E} \lesssim 0.14$, and $\Delta E \simeq 0.3$ eV. That this ΔE is comparable to the separation of the peaks in the σ_e curve can explain why this structure is partially suppressed in the σ_d data.

There are a number of interesting questions to pursue experimentally and theoretically. Collisions with $n \gg 1$ and $v_T/v_0 \sim 1$ will involve many coupled states and probably will be difficult to model. It will be very important to measure the n distribution in the final state. A more fundamental collision system would be e_R^--He; 35.4-keV $H(n)$ atoms would have the same velocity as free e^- near the 19.3-eV ^2S resonance in σ_e.[8] Finally, it will be very interesting to determine whether the Ramsauer minimum in σ_e for e^--Ar, -Kr, and -Xe collisions[16] will show up as a minimum in σ_I for D(high n) collisions with the same targets.

The author wishes to thank J. Bowlin for setting

up the microprocessor system and W. Lichten for a useful comment. This research was supported in part by the National Science Foundation Grant No. PHY78-25655 and by the A. P. Sloan Foundation.

[1]I.C. Percival and D. Richards, Adv. At. Mol. Phys. 11, 1 (1975); B. M. Smirnov, in *The Physics of Electronic and Atomic Collisions*, edited by J.S. Risley and R. Geballe, (University of Washington Press, Seattle, 1976), pp. 701-711; M. Matsuzawa, J. Phys. B 10, 1543 (1977); M. R. Flannery, Ann. Phys. (New York) 79, 480 (1973).

[2]P. M. Koch and J. E. Bayfield, Phys. Rev. Lett. 34, 448 (1975); G. F. Hildebrandt, *et al.*, J. Chem. Phys. 68, 1349 (1978); S. A. Edelstein and T. F. Gallagher, Adv. At. Mol. Phys. 14, 365 (1978); J. A. Schiavone *et al.*, Phys. Rev. A 16, 48 (1977).

[3]E. Fermi, Nuovo Cimento 11, 157 (1934).

[4]S. T. Butler and R. M. May, Phys. Rev. A 10, 137 (1965).

[5]Smirnov, Ref. 1.

[6]Preliminary results presented in P. M. Koch, Bull. Am. Phys. Soc. 22, 585 (1977), and 24, 580 (1979).

[7]D. Mathur and J. B. Hasted, J. Phys. B 10, L265 (1977).

[8]D. E. Golden, Adv. At. Mol. Phys. 14, 1 (1978), and references therein.

[9]Koch and Bayfield, Ref. 2.

[10]P. M. Koch, Phys. Rev. Lett. 41, 99 (1978).

[11]W. E. Lamb, Jr. and R. C. Retherford, Phys. Rev. 79, 41 (1950).

[12]J. E. Bayfield, L. D. Gardner, and P. M. Koch, Phys. Rev. Lett. 39, 76 (1977).

[13]P. M. Stier and C. F. Barnett, Phys. Rev. 103, 896 (1956).

[14]W. H. Thomason and D. C. Elbers, Rev. Sci. Instrum. 46, 409 (1975).

[15]P. M. Koch, to be published.

[16]E. W. McDaniel, *Collision Phenomena in Ionized Gases* (Wiley, New York, 1964), p. 118.

Optical Pumping between Levels of a Bistable State of Alkali Atoms Trapped in Rare-Gas Matrices

L. C. Balling, J. F. Dawson, M. D. Havey, and J. J. Wright
Department of Physics, University of New Hampshire, Durham, New Hampshire 03824
(Received 7 May 1979)

The results of pseudopotential calculations of the interaction of an alkali atom with its rare-gas neighbors in a solid matrix are presented. They can explain an interesting effect which appears to be due to optical pumping between two equilibrium positions in a bistable trapping site.

In the course of laser-excitation experiments[1,2] to study the absorption and emission spectra of Na and K atoms trapped in rare-gas solids at 10°K, we have discovered an interesting effect which appears to be due to optical pumping between levels of a bistable configuration of the alkali-matrix system. On the basis of pseudopotential calculations of the alkali–rare-gas interaction, the effect can be explained in terms of a model in which the alkali atom moves from one stable position to another within a trapping site in response to optically induced changes in the alkali–rare-gas potential.

Matrix-isolated alkali atoms exhibit a number of distinct absorption bands associated with $^2S_{1/2} \rightarrow {}^2P_{1/2,3/2}$ transitions in atoms located in different trapping sites.[1-8] The absorption of white light by Na atoms trapped in solid Ar, as observed in our experiments (Ref. 1), is shown in Fig. 1. This scan is in agreement with earlier work[3] on Na and is similar to absorption profiles in other alkali–rare-gas systems.[2-6] The absorptions due to different trapping sites are labeled with capital letters. Also shown in Fig. 1 is the

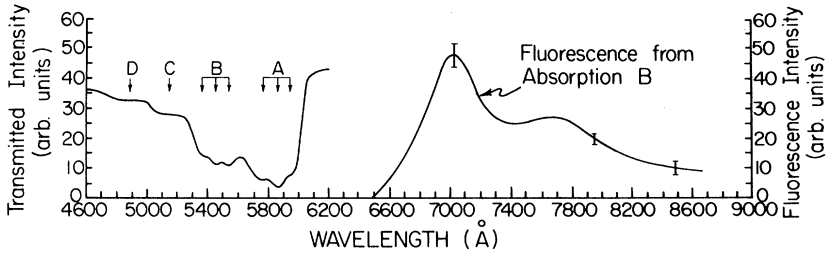

FIG. 1. A normalized scan of the absorption of white light by Na atoms trapped in solid Ar at 10°K. Also shown is the laser-excited fluorescence from absorption *B*.

