Observation of Direct Excitation of High-Orbital-Angular-Momentum High-Rydberg States by Threshold-Energy Electron Collisions

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Threshold-energy peaks are observed for electron impact excitation of N_2 and H_2 to high-Rydberg states. These peaks are attributed to the direct excitation of high-l states near threshold consistent with the prediction of Fano.

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The near-threshold behavior of electron-impact ionization was first described in terms of correlated motion of the receding electrons by Wannier.[1] Although many attempts were made to verify experimentally the predicted 1.127 power law of the threshold energy dependence, the first convincing demonstration was made by Cvejanovic and Read[2] in 1974. They not only measured a power law of 1.131 ± 0.019, but they also confirmed Wannier's other predictions, that the most probable angle between the two electrons is 180°, that near threshold the width of the angular distribution is proportional to $E^{1/4}$ where E is the excess energy, and that the energy distribution of each electron is constant over the range of possible values from 0 to E. It has been pointed out[3,4] that, if radial correlation is lost before ionization occurs, one electron will be trapped in a Rydberg orbital. Encouraged by the success of Cvejanovic and Read,[2] Fano[3] further examined the role of correlation in high-Rydberg (HR) state production and concluded that "high-l (orbital angular momentum) states are excited with substantial probability under electron bombardment with energies within a fraction of 1 eV of the ionization threshold."

The purpose of this Letter is to describe experimental observations of high-l HR states formed by *direct* excitation with near-threshold-energy electrons. These high-l HR states appear in the excitation functions as sharp peaks at threshold. There are two novel features to their observation in these experiments. The first is the use of a detector which is sensitive exclusively to states with principal quantum numbers $n \gtrsim 15$, i.e., HR states. The radiative lifetimes in HR states are similar to those of the hydrogen atom; they are on the time scale of microseconds, functions of l, and proportional to n^3 for fixed l. The second novel feature is the use of *molecular* HR states to filter out low-l states, or at least to attenuate them. On the time scale of the experiment, 100 μsec, decay of low-l HR molecules occurs much more quickly by predissociation or autoionization than it does by radiation. In high-l states, however, rates of autoionization and predissociation are greatly reduced because the centrifugal barrier prevents the high-l electron from interacting with the core.[5] Thus, low-l states are preferentially lost in this experiment and only high-l states, the ones of interest, remain to be detected. While low-l HR molecules produced by electron or photon impact could be promoted to high-l states by subsequent collisions with another electron or molecule, the time between collisions is typically $\sim 10^{-7}$ sec. In many cases, the initially excited low-l HR molecules have ample time to predissociate or autoionize before this *stepwise* excitation to high l can occur.

Several previous reports of *direct* excitation of high-l states are not totally convincing. Heideman *et al.*[6] report a broad oscillatory structure in the excitation cross section for helium 3^1D near the ionization threshold, as observed by the emitted light. Although Kocher and Smith[7] claim to have observed direct excitation of high-l states in the lithium atom, their results are more consistent with stepwise excitation.[8] Fano[3] interpreted the cusp in the scattered electron current for small excess energies, seen by Spence[9] and by Cvejanovic and Read,[2] as a manifestation of electron correlation and considered the possibility that high-l states are formed in this region. Finally, Heddle[10] assigned structure in the $3d$ He optical excitation functions to cascade from high-l states.

The apparatus and the experimental techniques used here to produce H_2 and N_2 HR molecules have been employed previously to study excitation of HR atoms from ground-state atoms[11,12] and from molecular dissociation.[13] A 40-μA electron beam with ~ 350 meV energy half width passes through H_2 or N_2 at a pressure of $\sim 10^{-5}$ torr. The HR molecules formed travel 20.1 cm from the electron beam to the detector with

thermal velocity. The detector consists of a pair of grids with a $\sim 10^4$ V/cm electric field between them, followed by a particle multiplier out of the line of sight of the collision region. This arrangement causes field ionization of states with $n \gtrsim 15$ and counts the resulting positive ions, but strongly discriminates against other particles from the collision region.

Three different kinds of measurements have been made: (1) Time-of-flight (TOF) distributions, which peak at 68 and 245 μsec for H_2 and N_2, respectively, are consistent with molecular thermal velocities in the 435 °K collision chamber. (2) Principal quantum number distributions are measured by applying a variable, uniform electric field across the flight path, which ionizes and thereby removes from detection HR states with $n \gtrsim (6\times 10^8/F)^{1/4}$ where F is the electric field in V/cm. The small dependence on l of this relationship lies within our resolution of $\pm \sim 3$ n units. The resulting distributions, similar to those reported previously for the rare gases, peak at $n = 35$ for H_2 and $n = 29$ for N_2. Analysis of the curve shape by the method described in Refs. 11 and 12 gives an average lifetime for the detected HR states of $10n^3$ μsec for N_2 and $1.5n^3$ μsec for H_2. (3) Excitation functions (the relative excitation cross sections) for H_2 and N_2 with $15 \lesssim n \lesssim 80$ are shown in Fig. 1 for a 10 eV energy range about threshold. The threshold energies were carefully calibrated and agreed with their ionization potentials to within the 0.1 eV experimental error. Since the H_2 data were taken with a pulsed electron beam and only a signal with TOF longer than 56 μsec was accepted, the contribution from dissociative excitation, with a threshold at 18.1 eV, is nearly negligible although it is well defined in Fig. 1(c). The excitation function for H_2 molecules appears to consist of two independent features: a sharp peak at threshold and a broader feature at higher energy. The presence of two different features is demonstrated by varying the experimental parameters. The curve in Fig. 1(b) was measured at lowered current. To obtain the excitation function in Fig. 1(c) an electric field of 500 V/cm was applied across the flight path. Thus HR states with $n \gtrsim 33$ were removed and only signals corresponding to n from 15 to 32 were detected. The change in shape below 18.1 eV, where only molecular HR can be formed, is obvious. These changes are interpreted below. The excitation function for N_2 [Fig. 1(d)] shows no such variation with conditions and consists only of a threshold peak. The onset of dissociative excitation at 24.3 eV is strong because this measurement was made without TOF resolution. Background due to photons and metastables was measured by turning off the voltage between the detector grids and placing a field of ~ 1200 V/cm across the flight path. It was then subtracted from the total signal to give Fig. 1(d). Runs with a pulsed electron beam and TOF separation of the signals gave the same curve shape, but with a poorer signal-to-noise ratio due to the smaller duty cycle.

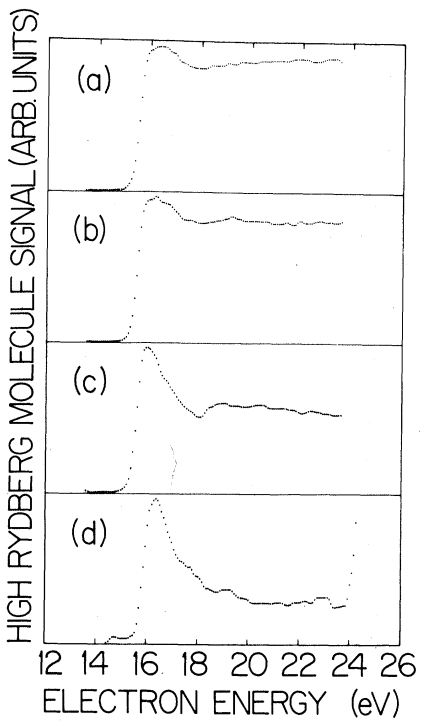

FIG. 1. Excitation functions for high-l, high-Rydberg states of (a) H_2, (b) H_2 with the electron current reduced from 40 to 20 μA, (c) H_2 for n between 15 and 32, and (d) N_2. Each curve represents about 16 hours of data accumulation followed by smoothing.

The three measurements just described prove that the detected signal is due to HR states. The arguments are as follows: The threshold is at the ionization energy, within experimental error; the TOF distribution is consistent with molecular thermal energies; and the electric field ionization data can be interpreted in terms of a reasonable n distribution. Other possible sources of the observed signal can be ruled out. Ions have the same threshold energy as HR states, but are prevented from reaching the detector by two pairs of deflecting plates with fields of ~ 15

V/cm and by the entrance grid to the detector which is biased +30 V with respect to the collision region. Even if ions were detected, their TOF should be significantly distorted by these electric fields from the observed near-Maxwellian distribution, and their known ionization cross sections[14] differ completely from the observed excitation functions. Photons, mostly far uv photons from the collision region, are observed, but can easily be distinguished by TOF discrimination. Electrons might escape from the collision region, but deflecting plates remove them and TOF distributions prove their absence. Metastable states exist for both H_2 and N_2, and those which survive at least one reflection to strike the first dynode are seen weakly as they were for helium.[11] However, their excitation functions are known[15] and differ substantially from those in Fig. 1.

The detected HR molecules must be in high-l states. This follows from the radiative lifetimes derived from n distributions. The effective lifetimes of $1.5n^3$ μsec for H_2 and $10n^3$ μsec for N_2, although they represent an average over some unknown l distribution, are comparable to those for $l=4$ and 10, respectively, for atomic hydrogen.[16]

Direct excitation of high-l states is indicated by the threshold peaks which are narrow as predicted by Fano.[3] A further indication of a direct process is the mere observation of any molecular HR signal. For N_2 a low-l HR electron with any core except the ground vibronic level can autoionize in $\sim 10^{-10}n^3$sec. The $X^2\Sigma$ $v=0$ core with a low-l electron can probably predissociate in $\sim 10^{-10}n^3$ sec since many repulsive states should cross it. A stepwise excitation of these low-l states to high-l states is unlikely because the rates of autoionization and predissociation for low-l HR states are fast compared to the time before a second electron collision. Only if the initial electron collision excites directly to a high-l state, will autoionization and predissociation be slower than the TOF of molecules to the detector and will HR signal be observed.

The H_2 molecule represents a special case because the $v=0$ level is not predissociated.[17] Thus H_2 provides the opportunity to compare directly high-l formation by direct and stepwise processes. The threshold peak in Figs. 1(a), 1(b), and 1(c) is assigned to direct high-l excitations.[18] The broad feature at higher energy is assigned to stepwise excitation to high-l HR states with a H_2^+, $v=0$ core. Reduced electron current [Fig. 1(b)] weakens the stepwise process more than the threshold peak because a direct process depends linearly on current whereas the stepwise process has been observed to increase more rapidly than linearly.[11,12] Detection of low-n HR states [Fig. 1(c)] also weakens the stepwise process. These observations demonstrate that the two processes yield different l distributions with direct high-l excitation producing higher l (i.e., longer lifetimes). These different l distributions explain why the measured effective l for H_2 at the threshold peak is lower than that of N_2; much of the H_2 signal at that energy is attributed to the underlying stepwise process.

We conclude that in this experiment the sharp peaks found at threshold are due to high-Rydberg states with large orbital angular momentum excited directly by single electron collisions. Such peaks should be present for the formation of any HR state, but they may be hidden beneath the much stronger signals for stepwise excitation to high-l states.[11,12] The key to observing them here is that, in molecules, autoionization and predissociation eliminate most HR signal other than that from direct excitation of high l. The mechanism proposed by Fano[3] for high-l formation is consistent with the observations, although the threshold peaks might also be explainable in terms of shape or Feshbach resonances. Ways to distinguish among these mechanisms, or perhaps to relate resonance theories to the concept of correlated electron motion near threshold, are neither obvious nor trivial. The theoretical work needed to form a unified picture lies beyond the scope of this experimental Letter. Finally, it should be pointed out that the l distribution has not been measured. This could possibly be done by deflecting a beam of high-l HR states in an inhomogeneous magnetic field. Neither has the shape of the excitation cross section been measured. A much higher resolution electron beam should be used, although this would necessitate a smaller current and hence a considerably smaller signal.

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[1]G. H. Wannier, Phys. Rev. 90, 817 (1953).

[2]S. Cvejanovic and F. H. Read, J. Phys. B 1, 1841 (1974).

[3]U. Fano, J. Phys. B 7, L401 (1974).
[4]A. J. Smyth, P. J. Hicks, F. H. Read, S. Cvejanovic, G. C. M. King, J. Comer, and J. M. Sharp, J. Phys. B 7, L496 (1974).
[5]Y. Band, J. Phys. B 7, 2072 (1974).
[6]H. G. M. Heideman, W. Van de Water, G. Nienhuis, and P. H. Peeters, J. Phys. B 9, L523 (1976).
[7]C. A. Kocher and A. J. Smith, Phys. Lett. 61A, 305 (1977).
[8]S. A. Edelstein and T. F. Gallagher, Adv. At. Mol. Phys. 14, 365 (1978).
[9]D. Spence, Phys. Rev. A 11, 1539 (1975).
[10]D. W. O. Heddle, Contemp. Phys. 17, 443 (1976), and Proc. Roy. Soc. London, Ser. A 352, 441 (1977).
[11]J. A. Schiavone, D. E. Donohue, D. R. Herrick, and R. S. Freund, Phys. Rev. A 16, 48 (1977).
[12]J. A. Schiavone, S. M. Tarr, and R. S. Freund, Phys. Rev. A 20, 71 (1979).
[13]J. A. Schiavone, S. M. Tarr, and R. S. Freund, J. Chem. Phys. 70, 4468 (1979).
[14]D. Rapp and P. Englander-Golden, J. Chem. Phys. 43, 1464 (1965).
[15]R. S. Freund, J. Chem. Phys. 51, 1979 (1969); W. Lichten, Phys. Rev. 120, 848 (1960).
[16]D. R. Herrick, Mol. Phys. 35, 1211 (1978).
[17]T. E. Sharp, At. Data 2, 119 (1971); C. Bottcher and K. Docken J. Phys. B 7, L5 (1974).
[18]A detailed interpretation of the H_2 threshold peak has not been included in previous reports. See, for example, H. Hotop, F. W. Lampe, and A. Niehaus, J. Chem. Phys. 51, 593 (1969); J. A. Schiavone, K. C. Smyth, and R. S. Freund, J. Chem. Phys. 63, 1043 (1975); H. Hiraishi, T. Kondow, T. Fukuyama, and K. Kuchitsu, J. Phys. Soc. Jpn. 46, 1628 (1979).

Observation of Structure in Laser-Induced Penning and Associative Ionization in Crossed-Beam Na + Na Collisions

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The results of double-laser experiments in which Na_2^+ and Na^+ are produced in crossed alkali beams under single-collision conditions in the presence of strong optical fields are reported. Structure in the mass-selected product ion intensity as a function laser frequency is observed when the optical field is strongly focused and tuned far off atomic or dimer transitions. These measurements are the first to show that the nuclear motion of the quasimolecular collision intermediate plays an important role in laser-induced collisional ionization.

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Laser-switched or laser-modified inelastic and reactive collisions are presently the object of intensive theoretical[1-3] and experimental study[4-7] because they offer the possibility of controlling both the relative and absolute probability of competing exit channels. The influence of the laser field is to modify the *electronic* states during the course of a collisional encounter. It is even possible to alter the outcome of a collision without a net transfer of energy between the atomic system and the radiation field.[8] In all cases "laser-induced" collisions are characterized by atomic field interactions which are nonresonant with respect to dipole-allowed transitions of the separated collision partners. It is important to distinguish these processes from multiphoton infrared absorption experiments in which nuclear motion absorbs photon energy directly. To date, observation of laser-induced energy transfer,[4,6] charge transfer,[5] and collisional ionization[7] have been established. We discuss here new results on Penning and associative ionization. With the optical-field intensity increased by over two orders of magnitude, we observe an entirely new domain of rich structural features. The observed collisions are

$$Na + Na \xrightarrow{\hbar\omega} Na_2^+ + e \quad \text{(associative ionization)},$$

$$Na + Na \xrightarrow{\hbar\omega} Na^+ + Na + e \quad \text{(Penning ionization)},$$

where the symbol $\hbar\omega$ indicates "in the presence of the laser field".

The crossed-beam apparatus is a high-vacuum cylindrical stainless-steel chamber in which two alkali atomic beam sources are mounted at right angles in a horizontal plane. Two laser beams enter from opposite ports, in the same plane and all four beams overlap in the interaction region at the chamber center. Kingston-Langmuir hot-wire detectors monitor effusive flux from the