Vibrationally Inelastic Scattering of High-n Rydberg H Atoms from N_2 and O_2

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The vibrationally inelastic scattering of Rydberg H atoms ($n = 30-50$) from N_2 and O_2 at $E_{coll} = 1.84$ eV was studied as a function of laboratory deflection angle. On average, 4 times more vibrational excitation was observed in collisions with O_2 than with N_2. Vibrational excitation of O_2 results largely from collisions in which an electron is briefly transferred from O_2 to the proton core, while the Rydberg electron remains a spectator. This provides further evidence that the free electron model applies to low energy collisions involving the ionic core leading to substantial momentum transfer.

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In collisions of high-n Rydberg atoms with nonpolar diatomic molecules such as N_2 or O_2, the dominant forces are of relatively short range and become appreciable only at distances 2 orders of magnitude smaller than the H ($n = 40$) Bohr radius of 848 Å. Since the velocity of a Rydberg H atom with $\sim$2 eV kinetic energy is only a factor of 3 smaller than the average orbital velocity of the Rydberg electron, the Born-Oppenheimer approximation, which assumes that electrons move rapidly relative to nuclei, does not hold. Consequently, the dynamics of Rydberg atom collisions with atoms and molecules are qualitatively different from those involving ground state or low-lying excited state species [1–4]. Such collisions have been described using the free electron [1–4] (or independent particle [5]) model, in which electron-target and ion core-target scattering events are treated independently. This model has its roots in Fermi's [6] explanation for observed line shifts in high-n Rydberg K atoms induced by the presence of inert gases at 1 atm pressure [7]. The subsequent developments in this field have been reviewed elsewhere [1–4]. Although there have been a few exceptions [5], the free electron model has been very successfully applied to a wide range of Rydberg atom scattering phenomena. Most notably, experimental cross sections for collisional destruction of Rydberg H and D atoms at high energies (keV) are equal to the sum of the cross sections for electron scattering and proton scattering [8,9]. Rydberg atoms at low velocities have also been used as a source of low energy electrons in studies of electron-molecule collisions at energies down to 4 μeV [10].

In the experiments noted above, the dominant interaction during the collision is between the nearly free Rydberg electron and the target molecule, with the ion core acting as a spectator. To date there have been very few measurements sensitive to events involving collision of the ion core [11–13]. Deflection of Rydberg Li atoms from several target gases was found to be in good quantitative agreement with core-target scattering, and, as expected, if the electron is a spectator, the cross section was found to be independent of the n level [11]. In an experiment by Boulmer *et al.* [12], collisions of ^{3}He ($n = 9$) with ground state ^{4}He produced fluorescence from both ^{3}He ($n = 9$) and ^{4}He ($n = 9$), indicating the occurrence of the "excitation exchange" process ^{3}He ($n = 9$) + ^{4}He ($n = 1$) $\rightarrow$ ^{3}He ($n = 1$) + ^{4}He ($n = 9$). This reaction involved charge transfer from ground state ^{4}He to the ion core of Rydberg ^{3}He. The Rydberg electron acted as a spectator and was carried off with the newly formed ^{4}He ion core while remaining in the $n = 9$ electronic state. A similar process was later observed in collisions of Rb isotopes [13]. Pratt and co-workers [14] studied the Rydberg molecule reaction $H_2^* + H_2 \rightarrow H_3^+ + e^-$ between the ion core of Rydberg H_2 and ground state H_2, with the Rydberg electron again acting as a spectator. These observations confirmed long-anticipated similarities between Rydberg core-molecule collisions and ion-molecule collisions [1]. This similarity suggests that high-n Rydberg atoms may be used to study ion-molecule scattering events at low collision energies without the usual complications of space charge effects.

In this study, we have scattered Rydberg H atoms from target molecules (N_2, O_2) in crossed molecular beams. Because the field ionization detector is sensitive only to Rydberg atoms with $n > 20$, our experiment provides direct insight into Rydberg atom-molecule collisions in which the scattered atoms remain in high-n levels. From conservation of energy and momentum, the velocity distributions of the scattered Rydberg atoms facilitate determination of the vibrational distributions of the target molecules as a function of scattering angle.

Our apparatus (Fig. 1) consists of two fixed separately pumped molecular beam sources crossing at 90° and a rotatable detector, all housed within a vacuum chamber ($P < 10^{-6}$ Torr). A monoenergetic H atom beam was produced by 248 nm photodissociation of pure hydrogen iodide (HI) in a pulsed molecular beam. The velocity of H atoms scattered perpendicular to the HI beam through a skimmer was either 19 130 m/s or 13 870 m/s, corresponding to production of H + I or H + I*, respectively. Either packet of atoms could be selected by appropriate delay between the photolysis and Rydberg excitation lasers. The H atoms were excited to a Rydberg level (denoted H*) $\sim$1.3 cm upstream of the collision region using resonant two-photon excitation via the H (^{2}P) state. Pulsed

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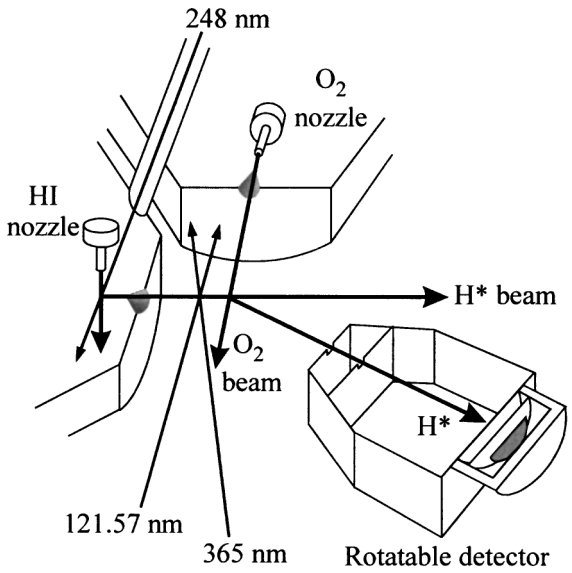

FIG. 1. Experimental apparatus.

vacuum ultraviolet radiation ($\sim 10^{12}$ photons/pulse, 5 ns, 30 Hz) at 121.57 nm was produced by resonance enhanced four-wave mixing [15,16]. A Rydberg level near $n = 40$ was accessed using tunable pulsed radiation near 365 nm ($\sim$5 mJ/pulse).

Scattered Rydberg H atoms were detected by field ionization in a detector chamber that may be rotated in the plane of the two beams. After traversing a distance of 29.2 cm, Rydberg atoms passed through a grounded fine-wire mesh and were field ionized by the electric field ($\sim$2 kV/cm) produced by a microchannel plate (MCP) detector. The signal was amplified and a multichannel scaler was used to measure the time-of-flight (TOF) distributions. A variable positive voltage (typically +30 V) applied to a second wire mesh located between the grounded mesh and the MCP rejected all positive ions formed prior to field ionization.

Representative TOF spectra are shown in Fig. 2 for H^* scattering from N_2 and O_2 at $E_{\text{coll}} = 1.84$ eV. Individual peaks correspond to excitation to different vibrational levels of the target molecules. A forward convolution program employing input center-of-mass (CM) translational energy and angular distributions for each vibrational level was used to simulate the TOF spectra at each laboratory angle [16]. This program averages over the known experimental parameters. The trial translational energy and angular distributions were iteratively improved until the simulations (solid line) agreed with the experimental data. The resulting vibrational energy distributions are plotted in Fig. 3.

At 20°, the scattering is primarily elastic with the dominant peak in the TOF spectrum appearing near $t = 16$ μs, resulting from collisions in which no vibrational excitation is imparted to N_2 or O_2 (Fig. 2). At wider laboratory angles, vibrationally inelastic scattering becomes more prominent. For O_2 peaks out to $v = 4$ are seen,

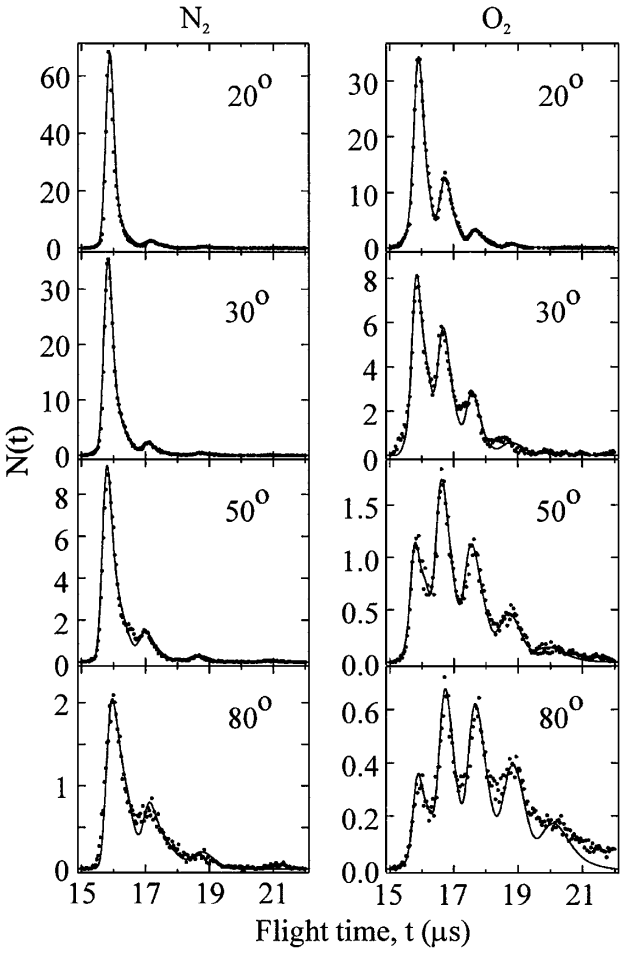

FIG. 2. Rydberg H atom time-of-flight spectra at indicated laboratory angles for N_2 and O_2 collisions at 1.84 eV. Solid lines are calculated TOF spectra based on optimized CM translational energy and angular distributions.

and at $\theta = 80°$ contributions from $v = 1$–3 are more intense than from $v = 0$. This is quite remarkable because translational to vibrational energy transfer in atom-molecule collisions is generally inefficient. Note that N_2 collisions lead to much less vibrational excitation with $v = 0$ dominant at all scattering angles.

The possibility of an n-level dependence in the collision dynamics was studied by comparing TOF spectra obtained by pumping to three different Rydberg levels ($n = 30$, 40, and 50). It was found that the shapes of the TOF spectra were identical to within the signal to noise level (10%), with no systematic change in the vibrational distributions as a function of n.

Because of the large transfer of linear momentum, the large-angle Rydberg atom deflection observed in this experiment must result from core-target scattering, rather than from electron-target scattering. The most striking observation is the much larger degree of vibrational excitation in O_2 than in N_2, despite the similarity in masses and vibrational frequencies. On average, there is a factor of 4 more vibrational excitation in O_2 than in N_2.

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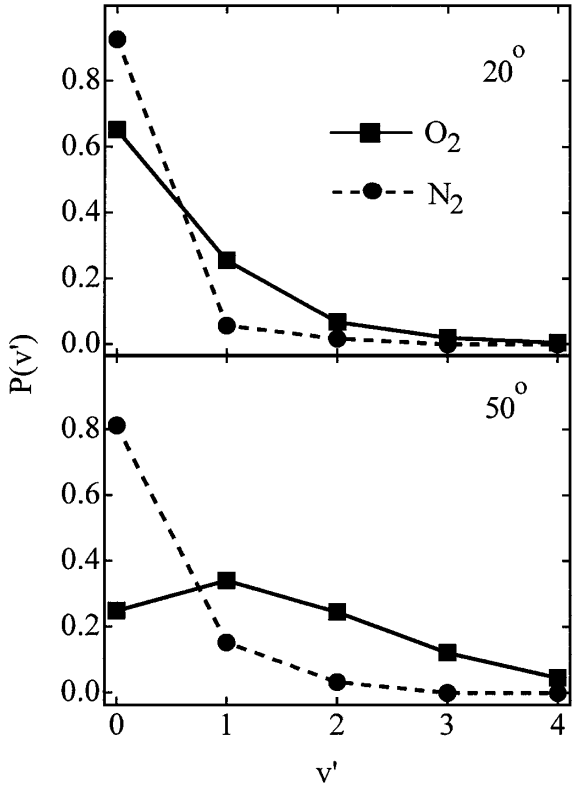

FIG. 3. Vibrational distributions for N_2 and O_2 from Rydberg H atom collisions at two different center of mass angles.

Similar "anomalous" vibrational excitation was seen by Gianturco *et al.* in the collisions of *protons* with O_2 at 9.8 eV and explained by a double charge transfer mechanism [17,18]. Using the free electron model, i.e., by assuming that collisions involve scattering of the proton core from O_2 with the electron acting merely as a spectator, we may apply the same mechanism to explain the large degree of vibrationally inelastic scattering of H^* from O_2 observed in our experiment.

The potential energy surfaces for $H^+ + O_2$ and $H + O_2{}^+$ cross at an internuclear separation of about 3 Å [Fig. 4(a)]. In a collision between H^+ and O_2, this crossing region is passed twice, each time with the possibility of adiabatic charge transfer, leading to four possible scattering processes [Fig. 4(c)]. Because our experiment is sensitive only to collisions resulting in no net charge transfer, the dominant contribution to the large vibrational excitation of O_2 involves charge transfer at *both* crossings. Because the highest occupied molecular orbital in O_2 has antibonding character, the equilibrium internuclear distance of $O_2{}^+$ (1.12 Å) is considerably shorter than that of O_2 (1.21 Å). This shorter ionic bond distance leads to increased Franck-Condon overlap with higher vibrational states of neutral O_2. Therefore, by accessing the $H + O_2{}^+$ surface briefly during the collision, although there is no net electron transfer, a considerable amount of O_2 vibrational excitation is induced. In $H^* + N_2$

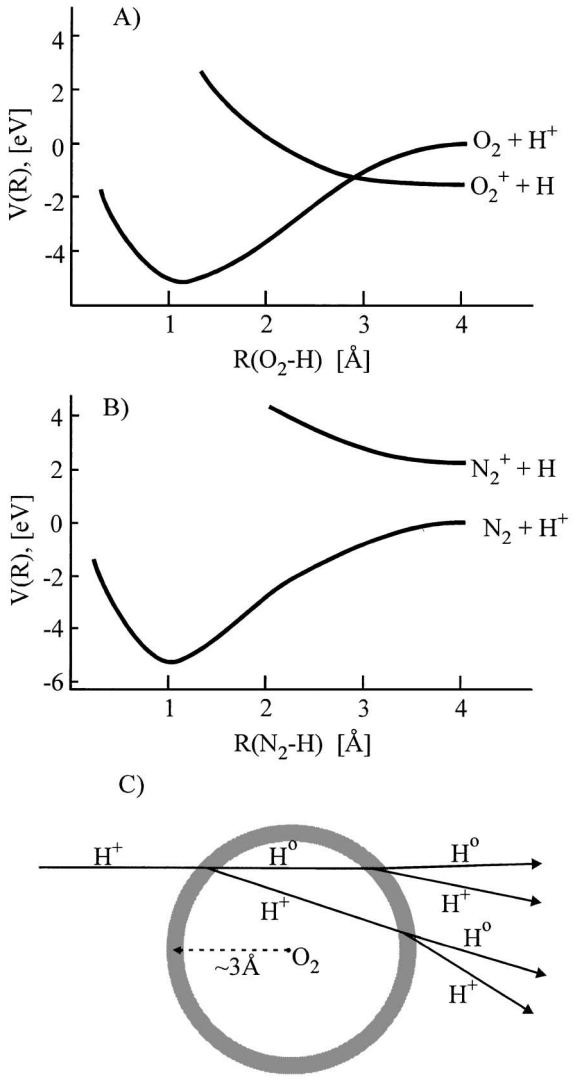

FIG. 4. (a) Potential energy curves for $HO_2{}^+$. (b) Potential energy curves for $HN_2{}^+$. (c) Four possible trajectories for H^+ scattering from O_2. Electron transfer may occur at $r \approx 3$ Å.

scattering, charge transfer is highly endothermic and cannot occur [Fig. 4(b)] [17,18].

According to Figs. 2 and 3, the degree of vibrational excitation of O_2 is substantially larger at $\theta = 50°$ than at $\theta = 20°$. This behavior may be qualitatively understood by recalling that wide-angle scattering results from small impact parameter (b) collisions. For $b > 3$ Å, electron transfer cannot occur, and the collision dynamics will resemble that for N_2. With decreasing impact parameters, the average time between curve crossings increases, leading to a greater change in $O_2{}^+$ bond length before reverse electron transfer, thereby inducing greater average O_2 vibrational excitation. For collisions at 1.84 eV, the distance between crossings ($\leq$6 Å) is traversed in $\leq$30 fs, a period of time only slightly shorter than the O_2 vibrational period. In the proton scattering experiments carried out at higher collision energies, the time between crossings was substantially smaller than the O_2 vibrational period.

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Consequently, a simple quantitative comparison of the vibrational excitation seen in Rydberg H atom scattering to that in proton scattering is not possible.

As expected, the integrated signal intensities (and therefore scattering cross sections) were found to be approximately the same for N_2 and O_2 under the same experimental conditions (Fig. 2). The H^+/O_2 collision cross section, calculated using the Langevin equation, is ~ 15 Å^2. To gain insight into the relative importance of wide-angle deflection of Rydberg atoms at 1.84 eV, we have carried our experiments in which the Rydberg excitation lasers were realigned to produce H^* in the interaction region, rather than upstream. Under these conditions, the observed H^* wide-angle scattering signal results from two sources: (1) collisions of H^* with the perturber molecule (as in the experiments discussed above) and (2) hard sphere collisions of ground state H atoms with target molecules followed by excitation to a high-n Rydberg state. The Rydberg atom number density was measured to be nearly the same in each experiment. Therefore, by subtracting the TOF spectra recorded with the laser upstream from those obtained with the lasers at the interaction region, the TOF spectra for ground state H atom hard sphere scattering may be determined. Interestingly, the integrated signal levels for Rydberg atom scattering and hard sphere H atom scattering were (to within a factor of 2) the same. By assuming the total cross section for H^+ core scattering to be 15 Å^2 (calculated using the Langevin equation), and that for hard sphere H atom scattering to be 4 Å^2 (calculated using the H Bohr radius and O_2 bond length), at least 25% of the Rydberg atom collision events involving the H^+ core remain in high-n levels after collision. Since Rydberg atoms are often thought to be "fragile," this might seem surprising. However, even for deflection through an angle of $\theta = 80°$, corresponding to $\Delta v \approx 25\,000$ m/s, the change of electron kinetic energy in the core's frame of reference is on average smaller than that required for ionization (0.085 eV for $n = 40$). Consequently, a substantial fraction of scattering events involving the proton core results in production of Rydberg H atoms that may be detected.

The striking similarity between wide-angle inelastic scattering of Rydberg H atoms from nonpolar molecules to that seen previously for protons is a further illustration that the free electron model, usually applied to scattering events involving the Rydberg electron, may be applied to low energy collisions involving the ionic core [11–13]. No n-level dependence in the dynamics was observed, as anticipated for a process in which the nearly free electron acts as a spectator. A practical application of this result is that Rydberg atoms may be useful for studies of low energy ion-molecule inelastic collision phenomena. The spectator Rydberg electron serves to neutralize the species under study, thereby avoiding the usual difficulties associated with space charge effects at low energies.

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