

Control of Diabatic versus Adiabatic Field Dissociation in a Heavy Rydberg System

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A novel phenomenon is observed in the dynamics of laser-prepared coherent wave packets, bound by the Coulombic $1/r$ potential of an ion-pair system. After exciting weakly bound (≈ 3 meV) H^+F^- wave packets in a Stark field, and permitting them to evolve in time, control of field dissociation via adiabatic and diabatic routes is demonstrated by applying delayed pulsed-electric fields, involving a zero-field crossing. Control manifests itself through the production of ions from each pathway at a different instant in time. This phenomenon is applied to map the oscillatory behavior of an angular momentum wave packet in a heavy Rydberg system. The characteristic frequencies of the observed Stark oscillations verify predicted mass-scaling laws for heavy Rydberg systems.

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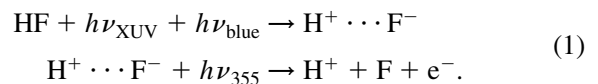
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Quantum states, confined within a $1/r$ Coulombic potential and forming Rydberg series associated with a principal quantum number n approaching infinity, have been extensively studied in atoms [1] and in molecules [2]. In the case of electronic Rydberg states coherent superpositions of manifolds of quantum states, originally alluded to by Schrödinger [3], have been investigated by ultrashort laser pulses, thus showing the temporal evolution of a wave packet along radial [4] or angular [5] coordinates. In molecules a $1/r$ potential not only results from the interaction between an ionic core and an electron, but can also result from the Coulombic attraction between charged parts of a weakly bound ion pair [6], which is further denoted as $A^+ \dots B^-$ for a diatomic molecule AB . The existence of bound quantum states below the ion-pair threshold was indirectly inferred from threshold ion-pair studies of oxygen [7], where it was demonstrated that weakly bound ion-pair states, or heavy Rydberg states, were long-lived, despite the fact that the energetic region of the ion-pair limit lies significantly above the ionization potential and various dissociation limits of the molecule.

Coherent wave packets of manifolds of heavy Rydberg states were recently demonstrated in the $H^+ \dots H^-$ system [8]. Although the experimental signal to noise was limited, monitoring of the wave-packet evolution of heavy Rydberg states in an electric field gave rise to characteristic Stark oscillations, the frequencies of which could be explained based on a model of the hydrogen *atom*, where the electron is replaced by the H^- anion. Later, generalized mass-scaling laws were derived, describing the energetics and temporal evolution of heavy Rydberg states, in terms of properties of electronic Rydberg states [9]. These scaling laws have not yet been subjected to experimental tests, except for the single case of $H^+ \dots H^-$.

In the present study the energetic region of the ion-pair threshold in HF, lying at $129\,558.2(3)$ cm^{-1} [10], is excited via two-step laser excitation. First, an extreme ultraviolet

laser (XUV), tunable near 95 nm, prepares an intermediate state; for reasons of optimum XUV yield we have chosen the $B^1\Sigma^+$, $v = 30$, $J = 4$ level at an excitation energy of $105\,937.38$ cm^{-1} [11] for this purpose. A second photon in the blue is obtained from one of two lasers: a tunable pulsed dye laser of bandwidth 2 GHz was used for recording overview ion-yield spectra, while a frequency-doubled pulse-amplified Ti:sapphire laser delivering pulses of 10 ns duration and less than 100 MHz bandwidth [12] was employed for the wave-packet experiments. Typical recordings of ion-pair and parent-ion-yield spectra are shown in Fig. 1. Both H^+ [Fig. 1(a)] and F^- [Fig. 1(b)] traces result from pulsed-electric-field-induced ion-pair dissociation, displaying resonances that often do not coincide with the photoionization process producing HF^+ parent ions [Fig. 1(d)] [13]. Additionally, for the first time, we demonstrate [Fig. 1(c)] through the use of a third, 50 ns delayed laser pulse, that an ion-pair yield spectrum in the bound region can be obtained via a photodetachment process:



This latter technique holds significant promise for the future, permitting heavy Rydberg systems to be probed at much larger binding energies and with more flexibility in terms of timing. The pulsed fields for the scans shown in Fig. 1 were typically applied a short time after excitation and with dc fields insufficient to discriminate against resonances above threshold, but clearly show resonances below threshold that are observed through field dissociation. Under small dc fields (<0.5 V/cm) the lifetime of the $H^+ \dots F^-$ system was approximately 200 ns, as evidenced by an exponential falloff with no structure. Under greater fields than these, lifetimes in excess of 10 μs were detected, and these were limited in part by flyout from the interaction zone.

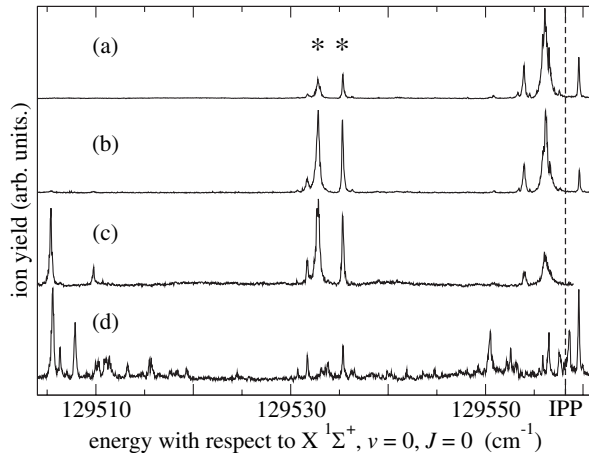


FIG. 1. Spectra in the region of the ion-pair production threshold (indicated by the dashed vertical line) in the HF molecule via 1 XUV + 1 VIS laser excitation, using a tunable pulsed dye laser (2 GHz bandwidth) in the second excitation step. The intermediate state is $B^1\Sigma^+$, $\nu = 30$, $J = 4$. (a) and (b) Spectra show field dissociation below threshold, detecting H^+ and F^- , respectively, at pulsed fields of 25 V/cm; (c) photodetachment spectrum, induced by an additional laser pulse at 355 nm and probing H^+ ; (d) photoionization spectrum detecting HF^+ . The resonances used to coherently prepare H^+F^- wave packets are marked by asterisks.

These observations reveal several properties characteristic to the HF molecule, which make it distinct from the H_2 molecule: (1) in H_2 [at least for the *gerade* manifold [8,9]] ion-pair states can be excited at any energy in the bound region, but in HF the ion-pair Rydberg series has significant oscillator strength only at some local resonances; (2) the ion-pair yield is of similar strength to the photoionization signal, a fact previously established [13], but in sharp contrast to H_2 , where the ratio of ion-pair yield to photoionization is less than 1%; (3) the lifetimes observed for heavy Rydberg wave packets in HF are much longer than in H_2 .

As a result of the resonance structure only specific energies are available for performing time-delayed field dissociation studies. In particular, the features lying 22.9 cm^{-1} and 25.4 cm^{-1} below the ion-pair threshold were used in the wave-packet studies. These wave packets, bound at $\approx 3\text{ meV}$, correspond to Rydberg states at principal quantum numbers of $n = 2900$ and 2750 . Excitation of HF at each of these two resonance positions was conducted under a constant electric field, F_{dc} , ranging in magnitude from 0.6 to 6.4 V/cm using the narrow-bandwidth pulse-amplified Ti:sapphire laser. This bandwidth results in excitation of Rydberg states with a spread of $\Delta n = 20$. After a predetermined time delay τ_d (ranging from 0 to 4 μs) an electric-field pulse with rise time 2.5 μs and magnitude 57 V/cm was applied to the interaction region with direction antiparallel to F_{dc} (see Fig. 2). Note that a three-plate ion-extraction configuration was employed (as drawn in the inset of Fig. 2) to obtain Wiley-McLaren space-focusing conditions [14]. The resulting

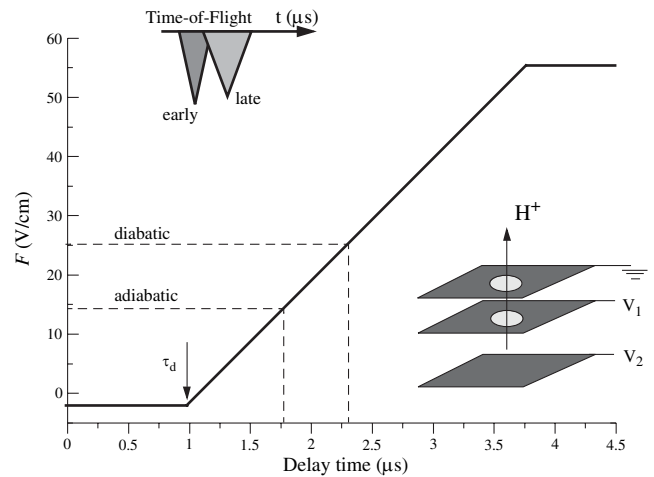


FIG. 2. An example of the electric field experienced by the H^+F^- system. τ_d represents the nominal point in time when the pulsed ramp is switched on. For the 22.9 cm^{-1} resonance the field required for pure adiabatic dissociation, as well as that corresponding to the onset for diabatic dissociation are shown by dashed lines. Inset upper left: a representation of the two time-of-flight peaks arising from these two processes: the *early* peak from adiabatic dissociation, and the *late* peak from diabatic dissociation. Inset lower right: the geometry of the three-plate extraction setup, where the upper plate is grounded to obtain Wiley-McLaren space focusing.

electric field is sufficient to dissociate the heavy Rydberg molecules, and two H^+ time-of-flight peaks were clearly visible: an *early* peak of width 150 ns, and a *late* peak of width 250 ns, separated by approximately 220 ns. This is in contrast to the single H^+ time-of-flight peak observed both when the pulsed field is parallel to F_{dc} and when this field has much shorter rise time. To confirm that these two peaks are not due to improper focussing, a variably delayed 355 nm photodetachment laser pulse was sent through the interaction region with intensity sufficient to photodissociate approximately one third of the ion pairs, resulting in a third peak of width 50 ns; this is consistent with free H^+ ions created during a small time interval under Wiley-McLaren space-focusing conditions.

We attribute the *early* and the *late* peaks to be due to principally adiabatic and diabatic dissociation, respectively. The field dissociation of heavy Rydberg systems is known to obey similar dynamics to that of the field ionization of electronic Rydberg atoms [15,16], and this behavior is described in detail in Ref. [1]. In the presence of an electric field F , the potential energy surface contains a saddle point, with energy $-2\sqrt{F}$ (in atomic units). For all Rydberg systems with nonpointlike cores the red and blue Stark states are coupled and at each (avoided) crossing there is therefore a finite probability of adiabatic or diabatic motion. For a heavy Rydberg system with binding energy E pure adiabatic dissociation occurs at an electric field given by $F_c = E^2/4$, which corresponds to 14.0 V/cm and 17.2 V/cm for the 22.9 and 25.4 cm^{-1} resonances, respectively. Conversely, pure diabatic disso-

ciation occurs over a range of electric fields greater than that at which the most redshifted Stark state is energetically allowed to dissociate (at $F_r = 4E^2/9$); higher Stark states are dynamically, rather than energetically, bound at this field strength [1,17].

Under our field conditions, if both adiabatic and diabatic dissociation pathways are available, ionic products from the former process will be created before those from the latter process. The difference in arrival time of these ions at the detector is dependent upon both differences in their creation times and their times of flight; this second effect will act to reduce the final difference in arrival time, because the products from diabatic dissociation experience a greater acceleration. We have numerically solved the equations of motion for ions created in the interaction region when the electric field in the interaction region reaches F_c and F_r at each resonance, and the results are in good agreement with experimental observations. As an example we show in Fig. 2 the electric field in the interaction region for $F_{dc} = 1.2$ V/cm and the relevant F_c and F_r fields for the 22.9 cm^{-1} resonance. In this case the difference in creation time is 540 ns, resulting in a final difference in arrival time within our spectrometer of 220 ns. As τ_d was increased the *early* and *late* peaks exhibited oscillatory behavior, while the sum of the two showed only an exponential decrease, indicating that there was controlled switching between principally adiabatic and principally diabatic field dissociation routes. A boxcar gate (SR250) was placed on each time-of-flight peak and each signal recorded for a range of τ_d from typically 0 to 4 μs , taken in a random order to avoid any systematic errors associated with drift of the lasers over time.

Figure 3 shows the observed time evolution for an angular momentum wave packet over about 30 periods, extending over as much as 4 μs . Presumably the observed decrease in coherence is an ensemble averaging effect, determined by the inhomogeneity of the electric field of a few percent; the lifetime of the $\text{H}^+ \dots \text{F}^-$ system as such is at least 10 μs , judging from the very slow decrease of total H^+ field dissociation signal. It should be noted that the total H^+ yield does not show any periodic structure whatsoever; this shows that the loss probability of the system during its evolution through low-angular-momentum states in the field, where collisions between H^+ and F^- could lead to molecular autoionization or dissociation, is low. The same can be concluded from the observation that in small-field conditions ($F < 0.5$ V/cm) delayed field dissociation has a decay constant of about 200 ns, corresponding to roughly 100 classical Kepler orbits of the H^+F^- system at the investigated binding energies (2.1 ns at 22.9 cm^{-1} and 1.8 ns at 25.4 cm^{-1}). This stability against decay is in contrast to the H^+H^- system, where such decay processes are the limiting factor of the lifetime of the weakly bound ion-pair state [8,9]. Experimentally Stark oscillation features were recorded for both resonances at a number of applied electric fields F_{dc} , and the oscillation frequency f is determined by fitting

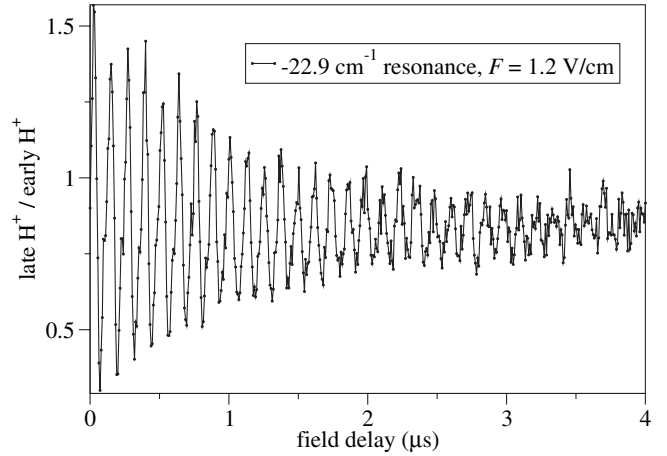


FIG. 3. An example of a recording of a pulsed-delay scan representing a Stark oscillation, detected by two-step laser excitation and pulsed field dissociation, and plotting the ratio of the early and late H^+ signals after the time-of-flight setup. Binding energy and dc-applied field as indicated.

the *ratio* of the peaks to the function $A(\tau_d) = A_0 \exp[-\tau_d/T_d] \sin(2\pi f\tau_d + \phi)$, with $A(\tau_d)$ and A_0 amplitudes, T_d the dephasing time of the wave packet, and ϕ an arbitrary phase.

The oscillation frequency f of an angular momentum wave packet at principal quantum number n in an electric field F is given by the linear Stark splitting: $2\pi f = 3Fn$. When quantities are expressed in usual atomic units, an additional mass-scaling factor must be included in the formulas for heavy Rydberg systems, resulting in $2\pi f = 3Fn/M$ and a modified Rydberg formula $E = -R_\infty M/n^2$ [9]. M is the reduced mass of the heavy Rydberg system in units of m_e , with $M(\text{H}^+\text{F}^-) = 1743.7058$. The theoretical frequency at binding energy E and field strength F is thus, with $F_0 = 5.142206 \times 10^9$ V/cm, the atomic unit of field strength and $\tau_0 = 1/(4\pi c R_\infty) = 2.4188843 \times 10^{17}$ s, the atomic unit of time:

$$f = \frac{1}{\tau_0} \frac{3F}{2\pi F_0} \sqrt{\frac{R_\infty}{ME}} = 30.4521 \text{ MHz} \frac{F/(\text{V/cm})}{\sqrt{E/\text{cm}^{-1}}}. \quad (2)$$

At the two fixed binding energies at which wave packets were investigated, the proportionality factors of f as a function of F are 6.36 MHz/(V/cm) at $E = 22.9$ cm^{-1} and 6.04 MHz/(V/cm) at $E = 25.4$ cm^{-1} . Figure 4 shows the oscillation frequencies as a function of electric field for both binding energies, together with the theoretical slope.

The data in Fig. 4 provide important physical information on the heavy Rydberg system. The extrapolation to zero field ($F_{dc} = 0$) yields in principle a value for the ion-pair threshold. For the data set of the 22.9 cm^{-1} resonance special care was taken to limit stray field variations (field stability better than 0.03 V/cm rms), but unfortunately the offset on the absolute value of the field strength may be as large as 0.1 V/cm. Accounting for an uncertainty of

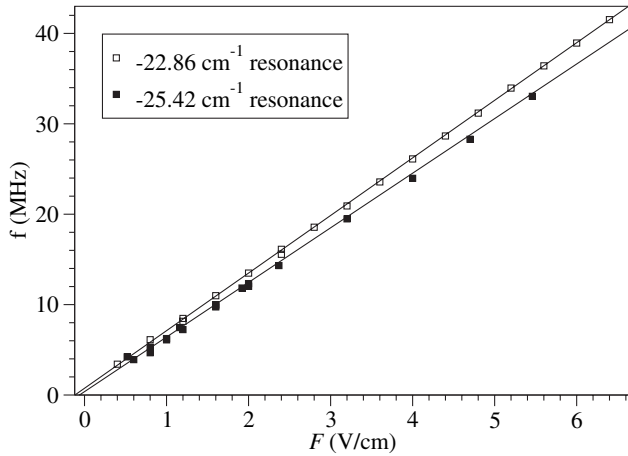


FIG. 4. Observed oscillation frequencies of the angular momentum wave packets as a function of applied dc field, F , during laser excitation for the two resonances indicated by an asterisk in Fig. 1. The line represents calculated oscillation frequencies via the mass-scaling equations, with an offset value determined in a fit.

0.05 cm^{-1} in the B - X transition [11] we obtain $E_{\text{IP}} = 129\,558.29(21) \text{ cm}^{-1}$ for the ion-pair threshold, in agreement with Ref. [10]. Improved measurement and control of the applied electric fields [18] would directly result in a more accurate value of the ion-pair threshold, and via thermodynamic cycles [9] also of other ionization/dissociation properties of molecules.

The agreement between theory and the data in Fig. 4 proves that the electric-field dependent Stark oscillation frequencies follow the mass-scaling law of Eq. (2). The mass-scaling laws for heavy Rydberg systems were derived in relation to observations in the H^+H^- system [9] and tested for the specific mass-scaling factor of $M = 918.5761$; now they are tested and found to produce perfect agreement for $M = 1743.7058$ (H^+F^-).

In the present study it has been experimentally demonstrated that the field dissociation pathway can be switched from following either a diabatic or an adiabatic route. This control only occurs when the dc field is antiparallel to that of the dissociation field ramp and therefore the total field passes through zero at a specific point in time. When this happens randomization of m takes place, and if the angular momentum wave packet has low- J character, m stays low, while if it has high- J character, m is more likely to become large. The nonpointlike core of a Rydberg system influences the ionization dynamics of low- m and high- m states differently, resulting in adiabatic ionization in the former case, and diabatic in the latter. Diabatic and adiabatic field dissociation therefore occur periodically, as seen in Fig. 3.

The different pathways of diabatic and adiabatic field dissociation result in ions formed at different times.

Control is established by varying the delay τ_d between the exciting laser pulses and the onset of a pulsed field ramp with a relatively slow rise time. Effective use of this control option results in high-contrast wave-packet oscillations and has verified the mass-scaling law for Stark oscillations. Other applications of this coherent control on the dynamical evolution of the wave packet may be envisioned. Manipulation and control of Rydberg wave packets is particularly promising for storage of quantum information [19].

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