Hydrogenlike Rydberg Electrons Orbiting Molecular Clusters

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Series of Rydberg states up to $n > 100$ are observed for the first time in weakly bound, polyatomic van der Waals clusters. Cross-correlation calculations of the dense spectra with simulated Rydberg series reveal a long-lived (μs), hydrogenlike series of Rydberg states. The slightly different series limits are interpreted as single quantum states in the dense rovibrational level manifold of the weakly bound cluster cation. [S0031-9007(98)06271-1]

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When an electron is moving in a Coulombic $-1/r$ potential of a positive point charge the bound energy structure can be described to a very good extent by the well-known Rydberg formula $E_n = -1/n^2$. While the hydrogen atom is one of the best examples of this charged pointlike core [For an overview, see [1] and references therein], similar Rydberg structures exist—and have been studied extensively—in other small core systems such as atoms (as recent examples, see Refs. [2–4]) or small molecules [5–13]. Inspired by the recent unexpected observation of resolved, high n Rydberg states ($n \approx 100$) in polyatomic molecules [14,15], the present paper focuses on high n Rydberg states of even larger molecular cores: Weakly bound, molecular van der Waals clusters such as the benzene $\cdot$ Ar complex. In these clusters, the center of charge and the center of mass do not necessarily coincide due to the strongly localized charge distribution on the cluster component with the lower ionization energy. This leads to a periodically moving center of charge for the Rydberg electron if the cationic core is undergoing rotations or slow intermolecular vibrations around its center of mass [16,17]. This is equivalent to a point multipole resulting from a transformation into a molecule-fixed rotating coordinate system with its origin in the center of mass [18]. Also, the classical time-scales for molecular rotation and slow intermolecular vibrations become comparable to the classical time-scale of the high Rydberg orbits leading to possible resonances between the very high density of core states and the Rydberg manifold. This has been thought to make the observation of individual Rydberg series in this energetic region at least questionable [17].

The experiments presented in this paper clearly prove the existence of very regular Rydberg series in weakly bound van der Waals clusters in the energetic region closely below and above the ionization threshold. They have been carried out by combining a narrow band optical double resonance excitation scheme with a selective field ionization detection of the Rydberg states [see Fig. 1]. The used laser setup and the molecular beam apparatus are similar to the one used in our recent coherent ion dip [19–21] and optical alignment [22] experiments: The necessary intense Fourier-transform-limited UV pulses ($\delta\nu_{\mathrm{FWHM}} < 70$ MHz) are produced by frequency doubling the pulsed amplified output of two cw single-mode ring lasers while the neutral cluster molecules are produced in a skimmed molecular beam of Ar seeded with 2% benzene. After excitation the Rydberg states are detected by field ionization which is based on the lowering of the ionization threshold by an applied static electric field. The range of n being ionized depends on the applied field; a rough estimate can be given by $\Delta E[\mathrm{cm}^{-1}] = \alpha\sqrt{E\ \mathrm{V/cm}}$, where α is in the range of 4 to 6 depending on the rise time of the field pulse [1,23]. In the presented experiment the Rydberg states are ionized by an electric field pulse of 180 V/cm which is applied with a variable delay ranging from 20 ns to 45 μs after excitation. This electric field pulse ionizes Rydberg states down to $n \approx 45$. In part of the experiments an additional prepulse of 0.5 V/cm and variable duration was applied after laser excitation and prior to the ionization pulse to remove prompt ions created during laser excitation and Rydberg states above $n \approx 200$. In both cases, no external fields are supplied during laser excitation. Using this pulsed selective field ionization scheme together with a mass selective time-of-flight spectrometer allows us to investigate Rydberg states in the energy window from $n \approx 45$ to $n \approx 200$ of a selected cluster species.

In Fig. 2 we present the first clearly resolved high n Rydberg spectrum of a van der Waals cluster of a polyatomic molecule and a rare gas atom. The measured ion signal at the mass of the cluster molecule is plotted against the total energy above the ground state of the neutral cluster. For the shown spectrum the rovibronic $S_1, 6^1, J'_{K'} = 3_3, (+l)$ intermediate state was used [24]. The high resolution spectrum in Fig. 2 reveals a

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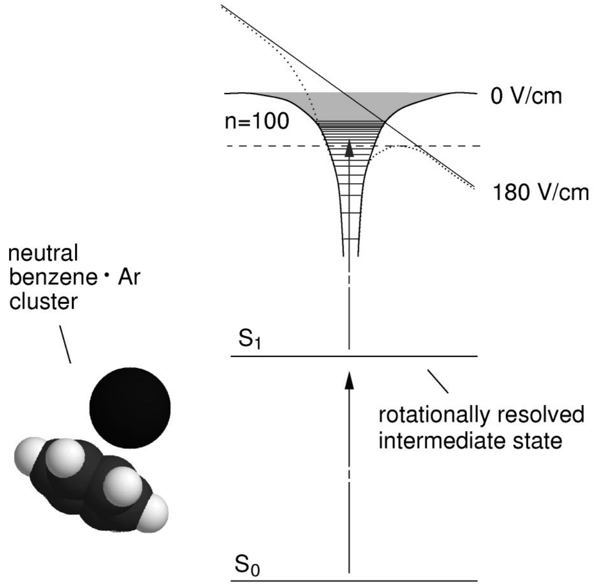

FIG. 1. Rydberg states ($n > 50$) of the benzene · Ar van der Waals cluster are excited by resonant two-photon excitation via selected rotationally resolved intermediate states in the first electronically excited state (S_1) and are detected by pulsed field ionization with variable delay between excitation and field ionization pulse.

complicated dense structure of long-lived (μs) states below the first ionization threshold. To check whether the spectrum can be understood as a superposition of a hydrogenlike Rydberg series converging to different states of the cationic core, we calculated the cross-correlation spectrum between the experimental spectrum and a simulated Rydberg spectrum with vanishing quantum defect. The result of this calculation is shown in the lower part of Fig. 2. Peaks in the cross-correlation spectrum indicate a good overlap between the simulated series and the experimental spectrum. The appearance of more than one peak in the cross-correlation spectrum indicates the existence of a corresponding number of Rydberg series in the measured spectrum. At least five distinct peaks appear in the cross-correlation spectrum shown in Fig. 2, marking the absolute positions of the different series limits with high accuracy [25]. Taking these series limits and assuming pure hydrogenic level-structure, it is now possible to simulate the experimental spectrum. The resulting simulation is plotted in the lower, inverted trace of Fig. 2. The relative intensities of the different series were taken from the amplitude of the corresponding peaks in the cross-correlation spectrum while no interseries coupling was taken into account. For better comparison with the measured spectrum the simulated stick spectrum in Fig. 2 is convoluted with a Gaussian filter with a constant width of 0.05 cm^{-1} (FWHM).

Without going into details of the rotational analysis, we like to emphasize that the cross-correlation spectrum represents the first *rotationally* resolved electronic ground state spectrum of the corresponding (benzene · Ar)$^+$ cluster cation. While a detailed rotational analysis, including the effect of the degenerate electronic ground state of the benzene chromophore, will be given in a forthcoming paper, we want to note that the slightly different series limits found in Fig. 2 can be interpreted as a J stack of angular momentum states with $2 \leq J \leq 6$ of the cluster cation. The relevant rotational constant is comparable with the rotational constant of the ionic benzene chromophore around its molecular axis and indicates that, as in the neutral cluster, the Ar atom is sitting close to the molecular axis of the benzene cation [15,26].

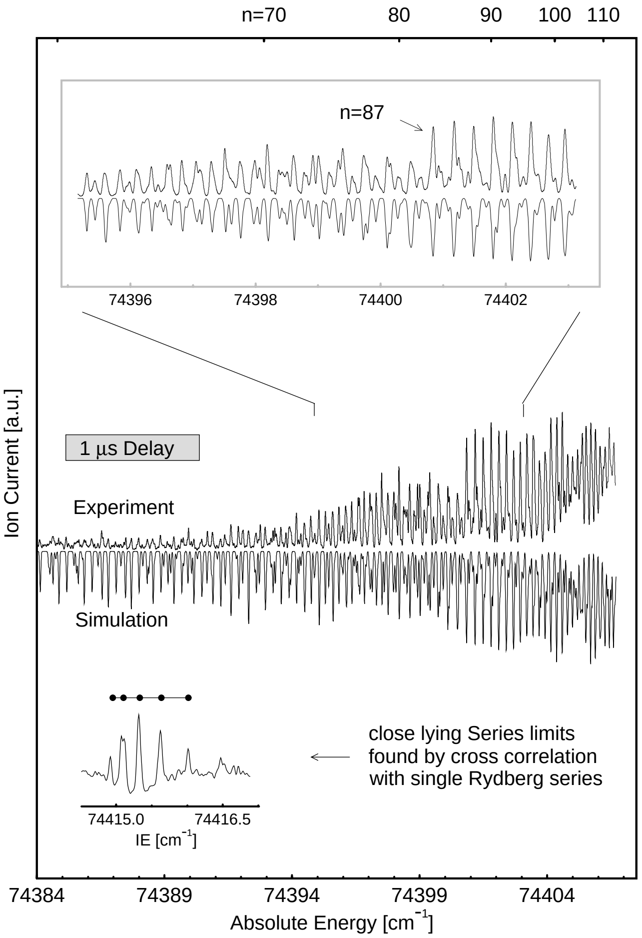

FIG. 2. Comparison of the observed spectrum converging to rotational states in the vibrational ground state of the (benzene · Ar)$^+$ cluster cation with a simulated spectrum (inverted) which consists of a pure additive superposition of five Rydberg series with different intensities converging to the series limits found in the cross-correlation analysis (The n values given on the top side of the frame refer to the strongest series.) In the lower part of the figure a spectrum is shown resulting from the cross correlation of the measured spectrum and a single Rydberg stick spectrum (amplitude scaled with n^{-3}), revealing the series limits of the overlapping Rydberg series.

Now we extend the investigated energetic region several 10 cm^{-1} above the lowest ionization energy. To avoid the high background of prompt ions produced in a direct ionization process, the two-step selective field ionization technique as described above was used. The delay time between the onset of the weak electric prepulse and the onset of the strong ionization field pulse was chosen to be 45 μs. No external field was applied during the laser excitation. Figure 3 shows the first experimental results on the resolved Rydberg series in this energetic range. In the lower trace (a), the Rydberg spectrum obtained by pumping via the $S_1, 6^1$ intermediate state is plotted. While taken with a much longer delay time, the spectrum shows a structure of dense Rydberg states similar to the one in Fig. 2. Besides the surprising result that even Rydberg states down to $n \approx 50$ survive the 45 μs delay time without decaying from the detectable n-range, the spectrum reveals another interesting detail: Although all prompt ions have been removed by the weak separation field, there is still some signal above the lowest ionization threshold. This very weak signal displays Rydberg structure and must originate from the Rydberg series converging to states representing slow relative motions of parts of the cationic core.

Taking spectra via an intermediate state with one quantum of the van der Waals stretching mode (motion of the benzene versus the Ar part of the cluster) excited allowed us to obtain Rydberg spectra converging to these states with a higher ion signal [see upper trace (b) of Fig. 3] [27]. Roughly, this spectrum consists of two energetic regions with series converging to limits at approximately 30 and 48 cm^{-1} above the lowest ionization energy. In both cases a pronounced resolved Rydberg structure with excellent signal-to-noise ratio can be recognized (magnified inset). This prominent Rydberg structure allows us to determine the series limits with the above mentioned cross-correlation technique with high accuracy. A closer analysis reveals that the rotational cationic level-structure obtained for the higher van der Waals vibrational mode is very similar to that of the vibrationless ground state, while the lower lying van der Waals level at 30 cm^{-1} exhibits a completely different rotational structure. This suggests that the higher lying van der Waals mode has the same symmetry as the ground state while the lower lying van der Waals mode has a different symmetry. The possible distinction of van der Waals modes with different symmetry will be a very useful tool for the understanding of the van der Waals level-structure of the (benzene $\cdot$ Ar)$^+$ cation which is complicated because of the high symmetry of the cluster [28,29].

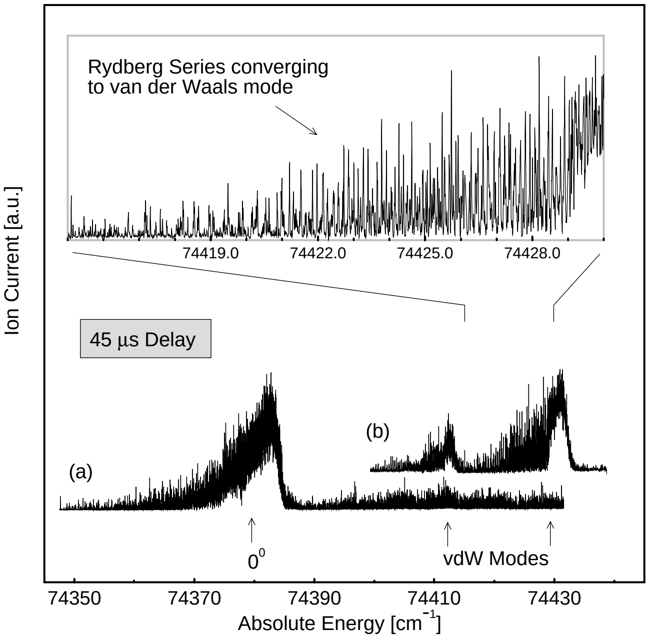

FIG. 3. Rydberg spectra of long-lived (μs) Rydberg states at and above the lowest ionization energy (delay between excitation and field ionization: 45 μs; prompt ions and Rydberg states above $n \approx 200$ are removed by a weak electric prepulse applied with 100 ns delay to the laser excitation): (a) excited via a pure benzene-skeleton mode in the intermediate state, (b) excited with one quanta of the van der Waals stretching mode excited in the intermediate state. Inset: magnified part of the Rydberg structure converging to rotational states in a totally symmetric van der Waals mode of the (benzene $\cdot$ Ar)$^+$ cluster cation.

In conclusion, the presented experiments led to the first observation of resolved Rydberg states in weakly bound, polyatomic van der Waals clusters very close to the ionization energy. Double resonance excitation with Fourier-transform-limited nanosecond UV-laser pulses and detection by selective field ionization reveals a rich structure of long-lived (μs) states in the high n range. Although classical time-scales for rotation of the core and Rydberg orbit time are comparable and a strong coupling of both degrees of freedom appears to be likely, the spectra resemble superpositions of only a weakly perturbed hydrogenlike Rydberg series. This can be understood in a picture of optically accessible states coupled by Stark mixing to the nearly unperturbed manifold of circular high l Rydberg states. A cross-correlation analysis of the measured spectra leads to rotationally and vibrationally resolved states of the investigated cluster ion. Measuring spectra via different intermediate rotational states allows us to map the rotational level-structure of the (benzene $\cdot$ Ar)$^+$ cation. First results indicate that the Ar atom is sitting above the center of the charged benzene ring as in the neutral cluster. We note that the $^2E_1$ electronic ground state of the cation is subject to Jahn-Teller distortion in the direction of an e_2 vibrational mode [30] and therefore a geometric interpretation of the rigid rotor fit constants has to be made with care. However, the rotational resolution achieved in our spectra will provide information on the Jahn-Teller coupling strength and on the importance of spin-orbit coupling of the unpaired electron in the ionic core of the cluster which has not been available so far. Concerning the possible Jahn-Teller and pseudo-Jahn-Teller couplings of van der Waals modes, it will be of major importance to include studies of combinations of skeleton modes of the benzene chromophore and van der Waals vibrations of the cluster constituents. From a dynamical viewpoint it is an interesting experimental result that even low lying Rydberg states with $n < 50$ can survive the long delay time of 45 μs which is explained by l mixing [13,31] during excitation due to electric stray fields present in our apparatus. The additional delayed prepulse of 0.5 V/cm enhances this effect particularly for $n < 50$. Although no strong frequency perturbations of the Rydberg series could be observed, the large separation between the center of charge and center of mass resulting in strong multipole moments of the Rydberg core suggests the existence of various effects on the observable long (μs) time-scale of the experiment. More sophisticated detection schemes such as multistep selective field ionization or time-delayed photoexcitation of the core with subsequent fast autoionization [32] will be promising tools to address this question in future experiments.

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