

Dissociative recombination of cold OH^+ : Evidence for indirect recombination through excited core Rydberg states

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The dissociative recombination of ground state OH^+ ions with electrons has been measured, using the heavy-ion storage ring technique. A comparison of the cross section to recent theoretical results reveals that several observed resonances are due to a type of indirect dissociative recombination involving Rydberg states with a bound excited ion core.

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The OH^+ molecule studied here has been detected in various comets and planets, and is one of the primary ion species leading to the production of H_3O^+ in interstellar clouds [1,2]. H_3O^+ is supposed to be the principal source of water in these clouds, and as such the understanding of the chain of reactions leading to its production is of importance. Among the reactions involving OH^+ , dissociative recombination (DR) plays an important role.

During the last few years, a new method has emerged that has made it possible to study this process under conditions coming close to their natural situation, i.e., for vibrationally cold molecular ions. The heavy ion storage ring merged beam technique [3] allows for the storage of molecular ions for a long period of time (seconds) during which they can radiatively relax to the ground vibrational state ($v=0$). With the ions being all in $v=0$, a comparison between experimental results and theoretical calculations is possible. This was not the case for many previous experiments where the vibrational population could not be determined [4].

In this Rapid Communication, we present a storage ring measurement of the DR of vibrationally relaxed OH^+ , together with a direct comparison with recent theoretical results. In particular, resonances are found in the DR cross section that were neither included in the prior theory nor observed in a previous single pass merged beam experiment [5]. An interpretation of these structures is given in terms of a transition to Rydberg states with an excited ionic core. This is an experimental indication that such a process, which was predicted a few years ago [6], is of importance for molecular ions with low lying excited states, such as CH^+ , N_2^+ , OH^+ and others. The enhancement of the DR cross section due to some of the structures observed here may be of considerable importance for the DR rates used in modeling interstellar clouds and planetary atmospheres.

The dissociative recombination of OH^+ , which can be described as



where OH^* is an excited neutral state, has already been investigated previously using a merged beam setup [5], but no efforts were made to vibrationally cool the ions that were produced in a radio frequency discharge ion source. The DR cross section was found to decrease with energy as E_{cm}^{-1} up to 1 eV, with a value of about $6 \times 10^{-14} \text{ cm}^2$ at $E_{cm} = 3 \text{ meV}$.

In the present experiment, a beam of 5.5 MeV OH^+ ions was produced by a TANDEM Van-de-Graaff accelerator: A standard sputter ion source with ZrH target and additional O_2 gas was used for the generation of negative OH^- ions with a peak current of about $5 \mu\text{A}$ in a pulsed mode. Two electrons from these ions were then stripped with N_2 gas at the high voltage terminal of the TANDEM accelerator. The stripping efficiency was only about 3%, i.e., the current of the positive ions was of the order of 150 nA. This beam was injected into the Test Storage Ring (TSR) at the Max-Planck-Institut für Kernphysik, Heidelberg. After injection, the beam was stored in a (ring-averaged) vacuum of $9 \times 10^{-11} \text{ mbar}$ with a beam lifetime of 7 s, and merged with the electron beam from the electron cooler. More details about the experimental setup can be found in previous publications [7,8].

The DR measurements were carried out by recording the associated rate as a function of the laboratory electron energy E_e , while the molecular beam energy E_i remained constant. After each injection, the ions were first stored to ensure vibrational and electronic deexcitation. After this cooling phase of 5 s, the electron acceleration voltage was stepped up to an adjustable value of E_e and switched back and forth at a rate of 10 Hz between E_e and a constant energy E_0 for normalization, where the DR cross section was negligible. Since the number of circulating ions was too low to be measured directly by the existing dc-current transformer, the rate coefficient was normalized to the background count rate at E_0 as in previous experiments [7,8]. The energy resolution in the center-of-mass system below $E_{cm} < 50 \text{ meV}$ is limited by the transverse energy spread of the electron beam of $k_B T_{\perp} = 17 \text{ meV}$ [9]. At higher energies the resolution is limited by the

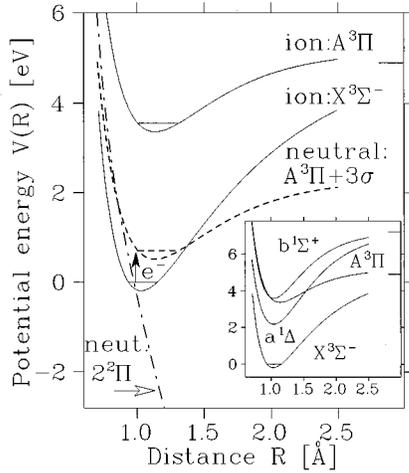


FIG. 1. Illustration of the indirect process via a Rydberg state of the low-lying excited state of OH⁺—A³Π for the vibrational quantum number $v=0$. The electron energy corresponds to 0.9 eV. The bound Rydberg state is drawn with the dashed line, the dissociating 2²Π state is drawn with the dot-dashed line [13]. As an inset the low-lying excited ion states are plotted [17].

longitudinal energy spread ($k_B T_{\parallel} = 1$ meV) resulting in a full width at half maximum given approximately by $\Delta E_{cm} = 4\sqrt{\ln 2} \sqrt{E_{cm} k_B T_{\parallel}}$ [10].

In order to measure the DR of the vibrational ground state of OH⁺, knowledge of the lifetimes of excited vibrational states is important. These values have been calculated [11]; e.g., the lifetime of the slowest $\Delta v=1$ transition ($v'=1 \rightarrow v''=0$) is predicted to be 4 ms. Thus, a short storage time of ≈ 200 ms is sufficient to fully relax the initial vibrational excitation produced in the ion source. Another possible problem is the presence of low lying electronically metastable states. These states are the $b^1\Sigma^+$ and the $a^1\Delta$ (see Fig. 1). The radiative lifetime of the first state has been calculated to be between 60 μ s and 100 ms [12], depending on the vibrational state, while no information about the lifetime for the second state could be found in the literature. In order to check for the presence of this metastable state in our beam, the DR cross section was measured as a function of storage time t_{inj} in the ring, up to 20 s. No differences in the value of the cross section were found after a storage time of 0.5 s; thus we conclude that either the lifetime of this $a^1\Delta$ state is shorter than 1 s or this state was not present in a noticeable fraction of our beam. We have assumed that this state does not have a lifetime that is considerably more than 20 s.

The experimental cross section $\sigma(E_{cm})$ for the DR of stored OH⁺ molecules, measured in the time window $8 \text{ s} \leq t_{inj} \leq 18 \text{ s}$ is shown in Fig. 2. In this figure, we also show the original as well as the convoluted theoretical results of Guberman [13] up to an energy $E_{cm} = 0.7$ eV obtained for ions in the rotational and vibrational ground state. The convolution, which reflects the experimental resolution, was carried out using a flattened Maxwellian velocity distribution [14] with $k_B T_{\perp} = 17$ meV and $k_B T_{\parallel} = 1$ meV for the transverse and longitudinal temperatures, respectively [10]. The experimental cross section is a relative cross section averaged over the energy resolution described above, and has

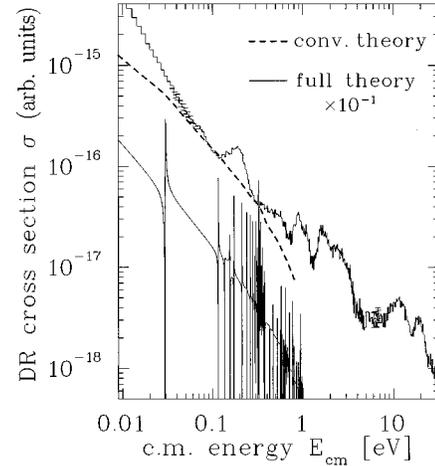


FIG. 2. Experimental cross section of the DR of OH⁺($v=0$) and comparison with the theoretical cross section. The calculated cross section [13] (full line, reduced by a factor of 10) and its convolution with the experimental resolution (see text) (dashed line) are also shown. The experimental and theoretical cross sections were normalized at $E_{cm} = 0.1$ eV.

been arbitrarily aligned at 0.1 eV with the theoretical results. The very narrow resonances in the original unconvoluted theoretical cross section are due to indirect recombination [15], where an electron is resonantly captured into a vibrationally excited Rydberg state with the OH⁺ core in its electronic ground state; the neutral molecule then dissociates along the 2²Π repulsive state. A full description of the theory and the intermediate Rydberg states is given in Ref. [13]. The predicted width of the widest of these resonances is 3 meV. These resonances are too narrow to be detected with our present experimental resolution and are therefore washed out by the averaging procedure (dashed line in Fig. 2). No theoretical calculation exists for higher electron energy.

In the high energy region, $E_{cm} > 5.1$ eV (the dissociation energy D_0 of the ion [16]) dissociative recombination can occur through excitation of neutral Rydberg states with a repulsive ion core. From the theoretical calculation of the ionic potential curves [17], the peak at 8–15 eV [centered at 10.9(1) eV] is likely due to resonant capture into Rydberg states having one or several of the following repulsive cores: $5^3\Sigma^-$, $2^3\Sigma^-$, $3^3\Sigma^-$, $2^1\Sigma^+$, $1^1\Sigma^-$, $2^3\Pi$, $3^3\Pi$, $2^1\Pi$, and $3^3\Delta$. The peak at 16.0–21.0 eV [centered at 19.5(2) eV] is due to an excitation to Rydberg states with the repulsive cores: $3^3\Sigma^-$, $3^3\Sigma^+$, $2^1\Delta$, $3^1\Pi$, and $3^1\Sigma^+$. The widths [6.6(5) eV and 7.3(5) eV full width at half maximum (FWHM), respectively] of these peaks arise from the superpositions of contributions from several states. For each state, the shape of the cross section is due to the Franck-Condon factor between the vibrational ground state wave function and the continuum wave function for the dissociative state. The shape is determined by the slope of the latter state and the variation of the electron capture width with internuclear distance. Such transitions, which are of the *direct* DR type, have already been observed in HD⁺ [7], CD⁺ [8], and others.

For the low-energy range, structures can be seen in the experimental DR cross section (Fig. 2), which are neither

reproduced by the theory (below 1.0 eV) nor have been observed in the previous merged beam measurement [5] performed with vibrationally excited ions. Another difference is the slope of the cross section at low energy (below 0.1 eV), which is very close to E_{cm}^{-1} for the theoretical calculation and approximately $E_{cm}^{-1.5}$ for the experimental results. Since the theory includes all relevant resonances caused by the indirect DR via vibrationally excited Rydberg states with the ionic ground state, it can be ruled out that the observed structures are due to this process.

In order to explain the low-energy resonances dominating the cold-ion spectrum, we propose a *different* type of indirect DR in which the electron is captured into Rydberg states having *electronically excited and vibrationally bound* ion cores. This indirect process has two very important characteristics that distinguish it from ground-state-core indirect recombination. First, capture can occur into $v=0$ Rydberg levels. If ground state ion and excited ion core Rydberg potential curves are nearly parallel, $v=0 \rightarrow v=0$ capture will have large Franck-Condon factors compared to the much smaller factors expected for $\Delta v \neq 0$. The possibility for high Franck-Condon overlap may lead to high values for the matrix elements describing the strength of the electron capture process. The second important feature is that capture into these Rydberg levels can occur by an electronic mechanism that is similar to that which controls direct recombination, possibly also resulting in a large matrix element. This type of indirect DR was already thought to be responsible for the low lying resonance observed in CD^+ at 0.8 eV [8], but because of the lack of theoretical calculations of the indirect DR into ground state core Rydberg states at this energy, this latter process could not be ruled out in the interpretation of the experimental spectrum. The possibility that such a process can be important was pointed out by Guberman [6], but it has not yet been included in any theoretical calculation of the DR cross section.

In order to be predissociated by the $2^2\Pi$ dissociative state shown in Fig. 1, the Rydberg states with excited ion core must also have $^2\Pi$ symmetry. For the low-energy peaks we consider Rydberg states formed from the $a^1\Delta$, $A^3\Pi$, and the $b^1\Sigma^+$ ion cores shown in Fig. 1. These three excited ion core states have T_0 values of 2.19, 3.45, and 3.60 eV, respectively [16]. Based on energies from preliminary calculations [18], the lowest-energy peak near 0.2 eV is due to a low lying π Rydberg orbital bound to the $a^1\Delta$ core. The

peak near 0.9 eV is due to a low lying σ Rydberg orbital bound to the $A^3\Pi$ ion core. The shoulder near 1.2 eV is very likely due to the $A^3\Pi$ core bound to a σ Rydberg orbital with a higher principal quantum number. The peak near 1.4 eV probably arises from a state similar to that causing the 0.9 eV peak, except that the σ Rydberg orbital has a higher effective angular momentum. At 1.4 eV, there may also be a contribution from a π Rydberg orbital bound to the $b^1\Sigma^+$ state. The shoulder between 2.2 and 4.0 eV may have contributions from several states, including a σ Rydberg orbital bound to the lowest-energy $^1\Pi$ ion core. All of these states are predissociated by $2^2\Pi$ completing the DR. Note that other dissociative mechanisms invoking dissociative routes other than $2^2\Pi$ may be possible, but they are likely to have slow rate constants due to a lack of favorable crossings. The observed low-energy peaks are only slightly broadened by the finite experimental resolution, which, for example, at 0.2 eV amounts to about 45 meV, while the observed width of the peak at this energy is about 120 meV.

To conclude, we have shown that indirect DR into vibrationally excited Rydberg states with the ionic ground state core is *not* responsible for the experimentally observed resonances. A comparison of the energy of the observed resonances with the position of Rydberg states with excited ion core shows that these states are likely to be sources of these peaks, through a new type of indirect process.

These processes are currently being included in the theoretical description [18] of DR, allowing for a more detailed understanding of the magnitudes, positions, and shapes of these resonances. Based on the above conjecture of the nature of these resonances, it is expected that excited core Rydberg states may be important in the DR of many molecular ions, such as CH^+ , N_2^+ , and O_2^+ . These processes can influence the rate coefficient as a function of electron temperature as well as the electronic state of the atomic products and could be important in models of planetary atmospheres.

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