New Resonances in the Dissociative Recombination of Vibrationally Cold CD^+

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(Received 8 December 1993)

The dissociative recombination of vibrationally cold CD^+ with electrons in the energy range of 0.01 eV to 60 eV has been measured using the Test Storage Ring in a merged beam arrangement. New resonance structures are observed with prominent peaks at 0.8 eV, 8.6 eV, and 11.7 eV. While the second and third resonance are readily attributed to direct recombination processes through Rydberg levels with dissociating molecular ion cores, the origin of the first resonance structure is not well understood, however, its small width of 0.45 eV is an indication of an indirect recombination process.

PACS numbers: 34.80.Gs

Although CH^+ was one of the first interstellar molecular ions to be observed in the visible part of the spectrum, its overabundance compared to theoretical expectations is still an unresolved problem [1]. The dominant process for removing CH^+ from the interstellar medium is the dissociative recombination (DR),

$$CH^+ + e^- \rightarrow C + H, \quad (1)$$

and as the temperatures of interstellar clouds are low, the main contribution comes from ions in their vibrational (v=0) and electronic ground state ($X^1\Sigma^+$). Several theoretical approaches have been used to calculate the DR of CH^+ in the low energy domain ($E < 0.3$ eV) [2]. Experimentally, the DR cross section was measured by Mul *et al.* [3] over an energy interval 0.03 to 0.4 eV, using an ion source with a paramagnetic buffer gas to quench the metastable $a^3\Pi$ state and a merged electron-ion beam technique. The measured cross section was found to be very large at low energy ($\sim 10^{-14}$ cm^2) and to follow approximately an $E^{-0.9}$ dependence [4] over the investigated energy interval, in good agreement with theoretical calculations [2]. However, some doubts remain about the population pattern of the vibrational levels built on the electronic ground state of the CH^+ in this experiment [4].

In this Letter we present a measurement of the DR of vibrationally relaxed CD^+ carried out over an energy range from 0.01 eV to 60 eV. In particular a new type of resonance, probably due to an *indirect* DR process, is found at 0.8 eV. This resonance influences the dissociative rate by collisions with thermal electrons, which is of capital importance for the understanding of the density of CH^+ in interstellar media. Moreover, this type of indirect recombination resonance probably also occurs in other molecular ions having excited bound potential energy curves in the energy range near 1 eV.

In order to produce vibrationally cold molecular ions, the new merging beam technique employing a heavy ion storage ring has been used. For molecular ions, a storage ring provides a very clean environment where a large amount of ions can be stored for a relatively long period of time (several seconds), thus allowing the deexcitation of electronic levels and the vibrational cooling by spontaneous transition between the vibrational levels. For the specific case of CD^+, the lifetimes of the vibrational-rotational levels of the $X^1\Sigma^+$ ground state have been calculated [5], and the average time for the vibrational cooling can be estimated to be on the order of a few seconds. The lifetime of the excited metastable $a^3\Pi$ has been estimated from calculations and measurements performed in other molecular ions [6] to be of the order of a second. Moreover, using the intense electron beam supplied by the electron cooler, electron-ion recombination and dissociation rates can be measured with good statistics and a resolution of about 0.1 eV over a wide energy range. This new technique has already been used successfully for the measurement of DR of HD^+ [7], H_3^+ [8], and HeH^+ [9].

In the present experiment, a beam of 2.0 MeV CD^+, with impurities such as CH_2^+, $^{13}CH^+$, or $^{14}N^+$ smaller than 3%, was supplied by a Van de Graaff accelerator using a standard Penning ion source filled with CD_4 gas, and injected into the Test Storage Ring (TSR) [10] at the Max-Planck-Institut für Kernphysik, Heidelberg. After injection, the energy was ramped up from 2.0 to 7.5 MeV by synchrotron acceleration in order to increase the ion beam lifetime, the density of the velocity matched electron beam, and to facilitate the detection of the neutral reaction products. The time required for ramping was 5 s. Up to 5×10^7 particles were stored in the TSR (circumference of 55.4 m) in an average vacuum of 1×10^{-10} mbar with a beam lifetime of 4.5 s. After reaching the maximum energy, the beam was merged with the elec-

0031-9007/94/72(13)/2002(4)$06.00

tron beam of the cooler over a length of 1.5 m. Typical values for the electron current were $\sim$ 10 mA inferring an electron density of $\sim 5 \times 10^6$ cm^{-3}. The electrons were guided by a 12 mT longitudinal magnetic field. A 40×60 mm Si detector was mounted straight ahead of the cooler section, at a distance of 6 m, to detect and to analyze the energies of the neutral fragments produced in the interaction region. In the energy spectrum, events recorded with the full beam energy correspond to the simultaneous detection of neutral C and D (or CD), and are thus due to a recombination process. Events recorded with 6/7 or 1/7 of the beam energy are due to the detection of a single neutral C or D, respectively, and are thus associated with the dissociative excitation process. Special precautions have been taken to avoid pileup from the excitation into the recombination channel.

The dissociative recombination measurements were performed by recording the associated recombination rate as a function of the laboratory electron energy E_e, keeping the beam energy E_i constant. In the center-of-mass frame the relative energy E is given by the relation

$$E = [\sqrt{E_e} - \sqrt{(m_e/m_i)\,E_i}]^2 \,, \qquad (2)$$

where m_e and m_i denote the electron and molecule mass, respectively. After each injection and acceleration, the molecules were electron cooled for 5 s in order to ensure equal velocity of ions and electrons and to reduce the diameter of the ion beam to $\sim$ 5 mm. The time for ramping and electron cooling (together 10 s) was long enough to allow for the deexcitation of the metastable electronic $a^3\Pi$ state as well as for the vibrational relaxation. After this phase, the electron acceleration voltage was increased to supply a certain electron energy E_e. In order to avoid any changes in the ion velocity the voltage was switched back and forth between E_e and the cooling energy at a rate of 11 Hz. By varying the energy level E_e from one injection to the next, a scan over the center-of-mass energy range from E =0.01 eV to 60 eV has been performed.

The relative rate coefficient $\alpha(E)$ for dissociative recombination was derived from the measured count rate by

$$\alpha(E) = \frac{r_{\mathrm{CD}}(E)}{A r_{\mathrm{CD}}(0)} \frac{1}{n_e(E)} \,, \qquad (3)$$

where $r_{\mathrm{CD}}(E)$ and $r_{\mathrm{CD}}(0)$ are the count rates in the DR channel at the center-of-mass energy E and at cooling energy ($E = 0$) respectively, $n_e(E)$ is the density of the electron beam, and A is a normalization constant. Since the number of circulating ions was too low to be measured directly, the rate coefficient was normalized to $r_{\mathrm{CD}}(0)$, which is directly proportional to the ion current. The experimental cross section was then evaluated as

$$\sigma(E) = \frac{\alpha(E)}{\sqrt{2E/m_e}} \,. \qquad (4)$$

No background correction was necessary since no full energy signals, associated with recombination induced by the residual gas, were observed when the electron cooler was switched off. The energy resolution in the center-of-mass system is about 0.1 eV and is limited by the transversal energy spread of the electron beam ($k_B T_\perp = 0.1$ eV), while the influence of the smaller longitudinal energy spread of $k_B T_\parallel = 1$ meV can be neglected at these energies. At small relative energies ($\simeq 1$ eV) the transverse energy component has the additional effect that the mean center-of-mass energy E is slightly larger than calculated by Eq. (2).

The experimental cross section $\sigma(E)$ for the dissociative recombination of CD^+ with electrons is shown in Fig. 1 together with the previous measurement of Mul *et al.* [3]. The absolute value of our measured cross section is normalized [through the constant A in Eq. (3)] to this previous measurement, taking into account the energy spread of the electron beam ($k_B T_\perp = 0.1$ eV and $k_B T_\parallel = 1$ meV as deduced from other recombination experiments at the TSR [11]). Corrections due to possible isotopic shifts are not included.

In the energy range from 0.01 to 0.2 eV, the DR cross section decreases as $E^{-0.9}$, in good agreement with the previous measurement [3] as well as with theoretical calculations [2]. For this energy the recombination proceeds via an interference between a direct process to the $2^2\Pi$

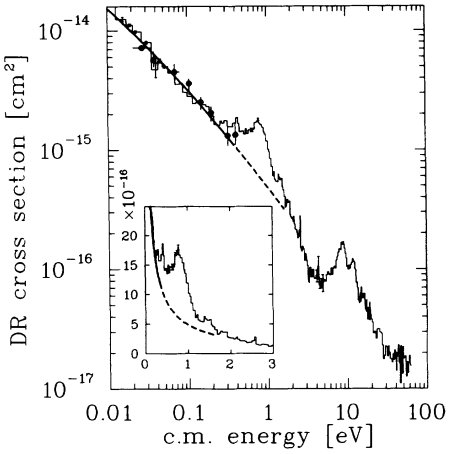

FIG. 1. Measured cross section of the dissociative recombination of CD^+ (histogram) with some characteristic statistical error bars. The full line indicates the $E^{-0.9}$ dependence of the cross section [2,4] folded with the flattened electron energy distribution ($k_B T_\perp = 0.1$ eV and $k_B T_\parallel = 1$ meV); the dashed line is an extrapolation to higher energies. Also shown is the previous measurement performed by Mul *et al.* [3] (dots), which has been adjusted to our electron energy distribution and has been renormalized by a factor of 0.5 in accordance to Ref. [4]. The present cross section is normalized to this measurement in the energy range between 0.01 and 0.3 eV. In the inset the DR cross section around the low energy structure is plotted on a linear scale.

state and indirect processes via the Rydberg states converging to the $X^1\Sigma^+$ ground state of the ion. However, at higher energies new resonances are found, which have not been discussed nor observed before: A prominent peak at 0.81(6) eV, which is accompanied by a smaller peak structure at $\sim$ 0.4 eV and a shoulder at 1.4(2) eV, and two peaks at 8.6(1) eV and 11.7(1) eV with a shoulder up to an energy of $\sim$ 20 eV. The peaks observed at higher energies can be attributed quite clearly to transitions to Rydberg states of the neutral CD^0 molecule characterized by quantum numbers n and l and different dissociating molecular ion cores (see Fig. 2). While the 8.6 eV structure is likely due to an excitation to the $c^3\Sigma^+$ ion core state and a capture of one electron in a Rydberg level with $n \geq 3$, i.e., to an excitation of $c^3\Sigma^+(nl)$ states of CD^0, the peak at 11.7 eV likely arises from an excitation to the $3^1\Sigma^+(nl)$ or $2^1\Pi(nl)$ states with $n \geq 3$. DR resonances of this type have been already observed in the DR of HD^+ [7] and HeH^+ [9]. The width of these resonances, measured to be 3.6(2) eV and 4.0(2) eV (FWHM), respectively, reflect the Franck-Condon factor between the ground state $X^1\Sigma^+(v = 0)$ wave function and the wave function of the dissociative level as well as the slope of this level as a function of the internuclear distance, and are of the expected size. The high energy shoulder is probably due to a high density of dissociating Rydberg states in this energy region. Theoretical calculations of the shape and the exact positions of these resonances are presently not available in the literature, but the simple fact that these resonances are observable as peaks in the DR cross section is a proof that the vibrational amplitude of the initial molecular ions must be small, i.e., that

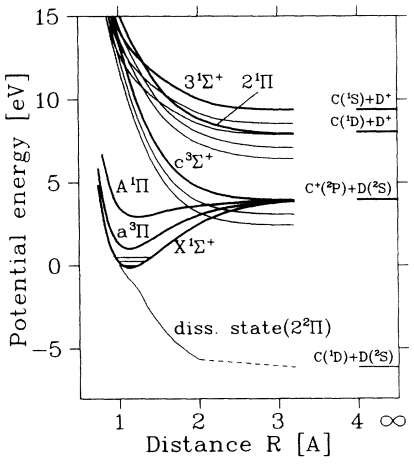

FIG. 2. Potential energy curves of the relevant CD^+ states (thick lines) and some excited states of CD^0 (thin lines). The ionic states are calculated in [12], while the associated Rydberg states are calculated by subtracting the hydrogen binding energy R/n^2 from this ionic states (plotted for $n = 3$ and 4). The dissociative state ($2^2\Pi$) of the neutral molecule is taken from Ref. [2]; other neutral states below the ionization threshold with bound character are excluded.

the ions are in low vibrational states. After injection and energy ramping, the DR cross section was measured for various time windows, but no changes of the widths of the resonances (including the low energy one) were observed in accordance with the expectation that the CD^+ molecules are electronically and vibrationally relaxed after a storage time of 5 s.

The low energy structure in the DR cross section is dominated by a narrow peak at 0.81(6) eV, which was not found in the previous measurement [3] (the cross section was measured only up to an energy of 0.4 eV), nor has it been anticipated in any theoretical calculation. The width of the peak amounts to only 0.45 eV, i.e., it is much narrower than the two previously discussed resonances. Thus, it cannot be the result of a direct transition to a simple dissociative state, unless the slope of this state would be very small in the region of the equilibrium distance of CD^+. However, such a state is presently not known. We have therefore tentatively assigned this resonance to an indirect, two step dissociative process, in which the electron is first captured in one of the Rydberg states of the neutral molecule having a low lying excited, but bound, electronic state of CD^+ as a core. The recombination is then followed by a dissociation along one of the dissociative states which couple to these Rydberg states. The recombination could be to a Rydberg state with the $a^3\Pi$ core, either with high n and little vibrational excitation (v), or with lower n but high v. Another possibility is the excitation to a low n Rydberg state with an $A^1\Pi$ ion core. In this case one would expect to see a Rydberg series starting with $n = 3$, but neither the position of the peak nor the interpretation of the shoulder at 1.4 eV as a limit of a Rydberg series is in quantitative agreement with this simplified picture of Rydberg molecules, where expected deformations of the potential energy curves for low main quantum numbers n are neglected. Candidates for the dissociative state are the $2^2\Pi$, already responsible for the DR rate at $E \sim 0$ eV, or possibly the $1^6\Sigma^-$ state calculated by van Dishoeck [13], which crosses both the $a^3\Pi$ and the $A^1\Pi$ Rydberg manifold. However, a strong coupling is not expected in the latter case because of the difference in the spin of these states. Although experimentally not excluded, a recombination without dissociation is unlikely as no stabilization mechanism fast enough to counteract autoionization is known.

Very narrow structures previously observed in the DR cross section below 1 eV with vibrational relaxed H_2^+ [14], N_2^+ [15], or NO^+ [16] were attributed to mainly destructive interferences of the direct and indirect recombination channels proceeding via vibrational excited Rydberg states with a ground state ion core. These interferences manifest themselves mainly by the occurrence of dips or "windows" in the cross section, because the probability for changing the vibrational quantum number by more than one is small [17] or because the opening of additional decay channels leads to higher autoioniza-

tion probabilities. (These structures are also predicted to occur in the DR of CD^+ below 0.3 eV [2], but they are smeared out in the present measurement because of the energy spread of the electron beam.) In contrast to these weak indirect recombination channels leading to destructive interferences, a transition to an excited molecular ion core is possible without changing the vibrational state, resulting in a higher capture probability, which may then turn out to be the dominant process and to lead to peaks in the cross section. The possible importance of indirect recombination processes via excited ion cores were already suggested by Guberman in the case of N_2^+ [18]. The existence of this type of resonance in CD^+ and likely in other molecular ions plays a crucial role for the dissociation rate in cold plasmas. With regard to the overabundance of CH^+ in the interstellar clouds, this increases the dissociation rate and therefore the discrepancy between predicted and observed ion density is made worse.

To conclude, we have measured the dissociative recombination of CD^+ with electrons between 0.01 and 60 eV, and observed the presence of three new resonance structures: While the two high energy structures can be interpreted as direct DR processes observed already in other molecules [7,9], the low energy resonance is tentatively attributed to an indirect DR process proceeding via a capture into one of the Rydberg states of the low lying bound electronic states of the ion followed by a dissociation along a state crossing these Rydberg states. It is expected that theoretical calculations for this new DR process will shed more light on the exact assignment of this resonance.

We would like to thank J. Linkemann, G. Miersch, U. Schramm, and Th. Schüssler for useful discussions and encouraging support during the beam time. For her kind interest and valuable discussions we would like to thank A. Giusti-Suzor. This work has been supported by the German Federal Minister for Research and Technology (BMFT) under Contract No. 06HD525I and by the German Israel Foundation (GIF) under Contract No. I-0208-202.07/91.

Note added.—During the referee procedure a new DR measurement has been carried out with an adiabatic expanded electron beam yielding a ~ 7 times lower transverse energy spread. The peak structure has been confirmed with higher resolution and better statistics.

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