

Near-Threshold Photodissociation of Cold CH^+ in a Storage Ring

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Photodissociation of CH^+ molecules ($\text{CH}^+ + h\nu \rightarrow \text{C}^+ + \text{H}$) is studied by collinear laser spectroscopy on a rotationally relaxed fast molecular ion beam in a storage ring. We have detected the resonances predicted between the thresholds related to the two fine-structure levels of the C^+ fragment for low initial rotations, and found that no heating processes hinder the complete rovibrational thermalization of the fast stored beam in a room temperature environment. [S0031-9007(98)05681-6]

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Studies of near-threshold photodissociation can relate to important open problems both in basic molecular physics and in neighboring disciplines such as astrophysics. A particularly interesting case is given by the photodissociation of CH^+ into C^+ and H fragments. This represents the reverse process of the radiative association $\text{C}^+ + \text{H} \rightarrow \text{CH}^+ + h\nu$, which has attracted considerable interest [1] as one of the possible production mechanisms of CH^+ in cold interstellar clouds. While the CH^+ molecular ion plays a central role in the chemistry of the interstellar medium, steady-state reaction schemes fail to explain its high abundance observed in diffuse interstellar clouds and production in shock-heated regions [2] has to be invoked. On the other hand, the required radiative association rates of C^+ and H atoms are not known from laboratory experiments and theoretical predictions are complicated by the specific level structure at the dissociation threshold, governed by the 63.4-cm^{-1} fine-structure splitting [3] of the $\text{C}^+(^2P)$ fragment energy levels (see Fig. 1). Since the CH^+ $A^1\Pi$ potential curve, responsible for the radiative transitions to the CH^+ ground state, is adiabatically correlated to the higher lying $^2P_{3/2}$ fine-structure level of C^+ , radiative association of cold ($\approx \text{meV}$ -energy) $\text{C}^+(^2P_{1/2})$ and H is expected to proceed through nonadiabatic coupling with other potential curves, largely via predissociating resonances between the $\text{C}^+(^2P_{1/2})$ and $\text{C}^+(^2P_{3/2})$ threshold energies [1,6,7]. While the low radiative association rates appear hardly accessible to direct laboratory measurements, the relevant predissociating resonances should be observable in experiments on the reverse, near-threshold photodissociation (process I in Fig. 1) if internally cold CH^+ molecular ions in low rotational states ($J \leq 15$) are used.

A number of detailed laboratory experiments [8] have studied CH^+ photodissociation close to threshold. Most data have been contributed by laser-ion-beam photofragment spectroscopy [9], a technique where molecular ions are produced in an ion source, accelerated to a few keV, and photodissociated by a merged laser beam [10]. On account of the high fragment detection efficiency and

the small Doppler broadening attainable with fast ion beams, this technique has been widely successful in studies both of molecular structure and of dissociation dynamics. However, the possibilities of controlling the internal excitation of the molecular ion beam are limited because ion sources usually produce “hot” molecular ions in highly excited electronic, vibrational, or rotational states. Therefore, regarding CH^+ photodissociation, shape resonances due to the centrifugal barrier [11] at high rotational excitation ($J \geq 15$) were observed and studied in much detail [12–14], whereas the fine-structure-related, Feshbach-type resonances of low- J molecules could not be detected.

Recently, MeV molecular ion beams have been stored in heavy-ion storage rings for tens of seconds, enough for many molecules to grant complete vibrational relaxation by infrared emission [15]. With this technique, dissociative recombination (DR) of vibrationally cold molecular ions and electrons has been studied extensively [16] and vibrational cooling has been clearly observed by probing

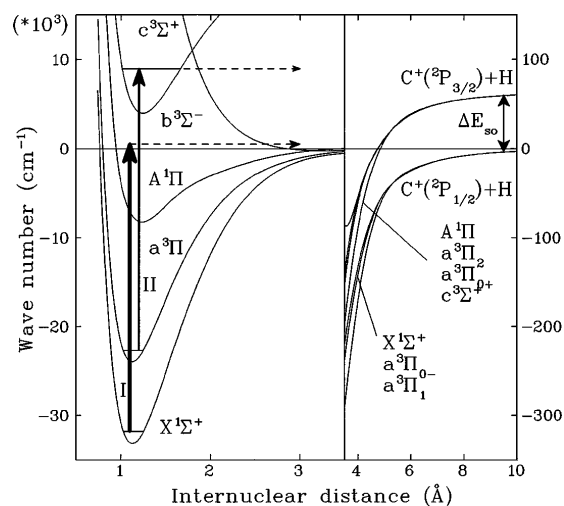


FIG. 1. *Ab initio* potential curves of CH^+ involved in the present experiment, from Ref. [4]. Spin-orbit-split curves (blowup with the scale on the right) are adapted from Ref. [5].

the kinetic energy release in DR [17]. Similarly, pure rotational radiative transitions should in principle yield rotational cooling of the stored fast ion beam and ultimately lead to a thermalization in the blackbody radiation field from the vacuum enclosure. On the other hand, rotational cooling is much slower than vibrational cooling and could thus be counteracted more easily by possible heating mechanisms such as MeV-energy collisions of the stored ions with the residual gas. So far, a detailed analysis of rotational level populations in stored fast ion beams has not been performed. In fact, such information can be of great help for the interpretation of many storage ring experiments; in particular, the rate of dissociative recombination is known to be sensitive not only to vibrational but also to rotational excitation [18].

In this Letter, we report a CH^+ photodissociation experiment in a storage ring. This new approach links photofragment spectroscopy to the storage ring technique and adds two great advantages. First, provided long storage, the molecules are internally cold. For CH^+ , this allows us to observe in detail the previously inaccessible low- J photodissociation spectrum. Second, before internal cooling is complete, the spectrum is strongly time dependent. Deriving from the spectrum the rotational level populations, we can monitor for the first time rotational cooling in a stored fast ion beam.

Our setup, similar in principle to a laser-ion photofragment spectrometer [10], uses the TSR storage ring [19] (Max-Planck-Institut für Kernphysik, Heidelberg, Germany) to store the molecular ion beam. CH^+ is produced from CH^- molecules created in a cesium sputter source and stripped in a tandem Van-de-Graaff accelerator. Every 30 s, typically 10^7 molecules are injected into the ring at an energy of 7.2 MeV and then circulate on a closed orbit (55.4 m circumference) defined by bending magnets with interleaved straight sections (each ≈ 10 m long). Collisions with the residual gas (mostly H_2 , $\approx 3 \times 10^{-11}$ mbar) decrease the beam intensity exponentially with a mean lifetime of 10 s. To photodissociate the ions, a pulsed, frequency-doubled dye laser beam (tuning range 300–330 nm, 10-ns pulses of 1-mJ energy at 200-Hz repetition rate) is merged with the ion beam along one of the straight sections. In the bending dipole behind the interaction region the C^+ fragments are mass separated from the circulating CH^+ beam and detected by a microchannel plate. Using a multihit time-to-digital converter to record the distribution of fragment arrival times relative to a preceding laser pulse, the photofragments are easily identified as a peak on a constant background of collision-induced fragments. [Additional C^+ “photofragments,” however, can arise from molecules excited to high-lying, yet bound rovibrational levels just below the dissociation threshold, which undergo field-induced dissociation in the motional electric field of 125 kV/cm acting in the mass-separating (1.21-T) dipole magnet.] The area of the photofragment peak, normalized to the ion beam

intensity and to the number of laser photons, is measured as a function of storage time t_s and laser photon wave number $\bar{\nu}$ (in the moving frame). As the number of photofragments was found to be proportional to laser intensity (no saturation), the normalized rate is proportional to the photodissociation cross section. Only a rough estimate is possible for the absolute cross section because the overlap between the laser and the ion beam could not be accurately measured. The Doppler shift was calculated from the velocity of the ion beam as determined from the ring circumference and a Schottky-noise measurement of the revolution frequency; the estimated uncertainty of the absolute photon energy is $\pm 2 \text{ cm}^{-1}$. The spectral resolution is approximately equal to the laser linewidth ($\Delta\bar{\nu} \approx 0.5 \text{ cm}^{-1}$), the velocity spread of the ion beam ($\Delta v/v \approx 10^{-4}$) contributing a minor broadening.

In a previous experiment at the TSR dedicated to the dissociative recombination of CH^+ [17], the ions were observed to be vibrationally cold ($v = 0$) after 2–3 s. Moreover, by measuring the intensity of some of the shape resonances previously assigned in the visible part of the spectrum [13] in an exploratory photodissociation experiment [20], high rotational levels ($J \geq 15$) were seen to be depleted after about 100 ms. The DR experiment also revealed that a substantial fraction of the ions ($\approx 60\%$ – 70% at injection) populate the $a^3\Pi$ metastable state. The radiative lifetime of this state was measured to be $(7 \pm 1) \text{ s}$ [17]. For the present work performed with the same ion source, this implies possible extra photofragments from photoexcitation of $a^3\Pi$ molecules to the $b^3\Sigma^-$ state, followed by predissociation via the $c^3\Sigma^+$ curve (process II in Fig. 1).

The laser was scanned around the $X^1\Sigma^+(v = 0, J = 0)$ dissociation energy, assuming the value $D_0 = (32907 \pm 23) \text{ cm}^{-1}$ (referring to the $^2P_{1/2}$ threshold) indirectly determined in an earlier experiment [13]. Figure 2(a) shows the full energy range, scanned with a stepwidth of 0.5 cm^{-1} or better, for short storage times in the interval $[0.4, 1] \text{ s}$. At these short times the spectrum is in fact dominated by the extra photofragments from process II; two red-shaded bands (2-0 and 3-0 of $b^3\Sigma^- - a^3\Pi$ [21]) are seen with heads around 32400 and 34100 cm^{-1} . Both bands have not been rotationally resolved before and will be treated in a future publication.

Near the expected dissociation energy [Fig. 2(b)] only a structureless continuum signal can be seen apart from some high- J resonances of the $b^3\Sigma^- - a^3\Pi$ 3-0 band. But this region of the spectrum changes dramatically with storage time: In Fig. 2(c), these resonances due to process II have completely disappeared because of rotational cooling within the $a^3\Pi$ metastable state; the continuum signal has started to shift to the right and new peaks emerge.

After about 15 s, the spectrum reaches a steady state shown in Fig. 2(d). The continuum now peaks around 32950 cm^{-1} , and the superimposed resonances turn out to be clustered to groups similar to each other, separated

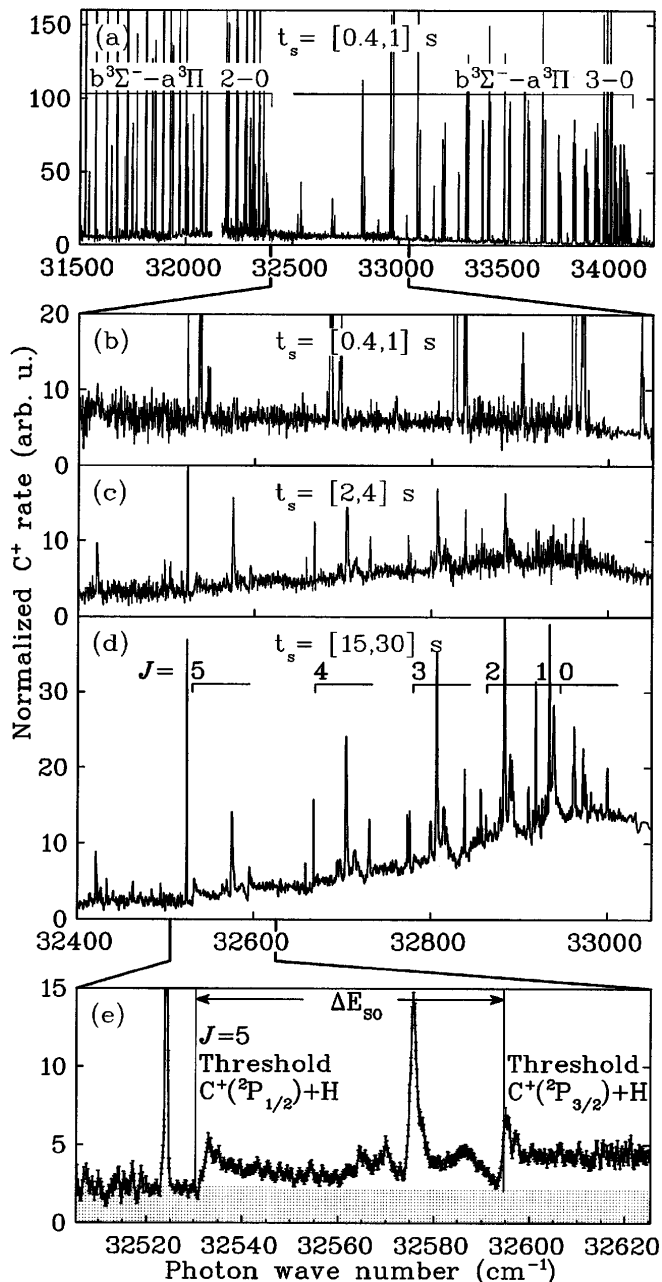


FIG. 2. Photodissociation spectrum for different storage times. The hot spectrum (a) displays two bands of the $b^3\Sigma^- - a^3\Pi$ system. As the ions cool internally, the near-threshold spectrum gradually builds up (b)–(d), revealing initial- J contributions as indicated. The resonances arising from $J = 5$ are shown in detail (e).

by flat sections that stepwise grow with energy. This is the spectrum of near-threshold photodissociation expected for $v = 0$, low- J rotational states, each contributing a resonance group followed by a continuous part. All resonances belonging to an initial state $X^1\Sigma^+(v = 0, J)$ are predicted to lie in the energy interval $[D_0 - E_J, D_0 - E_J + \Delta E_{so}]$, the relative positions of these windows being safely known from the initial rotational energies E_J [22] and the $C^+(^2P)$ spin-orbit splitting

ΔE_{so} [3]. The windows for $J = 0, \dots, 2$ overlap because $E_J - E_{J-1} < \Delta E_{so}$. The window pattern matches the observed resonance groups if initial J states are assigned as shown in Fig. 2(d). The contributions $J = 6, \dots, 9$ were also identified; they are partly interleaved with the low- J resonances of the $b^3\Sigma^- - a^3\Pi$ 2-0 band from process II, but time dependences greatly help in the assignment. Some very narrow resonances fall closely below the windows of width ΔE_{so} and are attributed to field-induced dissociation (see above) of weakly bound rovibrational levels. The dissociation energy consistent with the window pattern is $D_0 = (32947 \pm 5) \text{ cm}^{-1}$, slightly higher than the earlier indirect measurement [13]. The error given is dominated by the uncertainty in matching the pattern without exact knowledge of the expected resonance positions.

Figure 2(e) exemplarily shows a blowup of the resonance group arising from $J = 5$. The underlying continuum from $J > 5$ (hatched) was estimated by a linear extrapolation from the flat part below the assigned lower window limit. (A high narrow resonance attributed to field dissociation appears just below this limit.) At the present stage of theory, any detailed comparison to the experimental spectrum is hampered by the limited precision of the potentials assumed in the calculations [6,7]. Nevertheless, some patterns can be followed through the various J groups: The prominent peak at 32576 cm^{-1} has counterparts in each of the other groups, the energies of the final states matching a $BJ(J+1)$ law. The smaller peak at 32596 cm^{-1} is part of a similar series. Such resonances above the upper threshold can appear within the expected height of the centrifugal barrier ($\approx 2 \text{ cm}^{-1}$ for $J = 5$). Theory [6,7] predicts the strongest features to mark Q branch transitions to the $A^1\Pi$ curve, suggesting that the two series belong to the $A^1\Pi(v = 13, 14)$ vibrational states. Confirming the extensive close-coupling calculation [7], the resonances tend to be broader than predicted by the earlier perturbation treatment [6]. Moreover, the J groups reveal more peaks than can be accounted for by $A^1\Pi$ levels only. This supports the additional prediction of Ref. [7] that also rovibrational levels of the triplet states (see Fig. 1) appear as intrathreshold resonances by intensity borrowing from the main $A^1\Pi - X^1\Sigma^+$ transition. A complete assignment of the spectrum, however, requires a theoretical calculation based on optimized potentials and is presently under way. The estimated absolute cross section is about 10^{-20} cm^2 (at 33000 cm^{-1}), in agreement with theory [6,7].

The time dependence of the spectrum was used to study rotational cooling within the $X^1\Sigma^+(v = 0)$ state. The measured photodissociation cross section is a sum of state specific cross sections σ_J , weighted with the relative populations n_J . Qualitatively, a population transfer from higher to lower rotational levels is clearly marked by the piling up of the continuum signal [Figs. 2(b)–2(d)]. Quantitatively, by taking the functions $\sigma_J(\bar{\nu})$ from theory

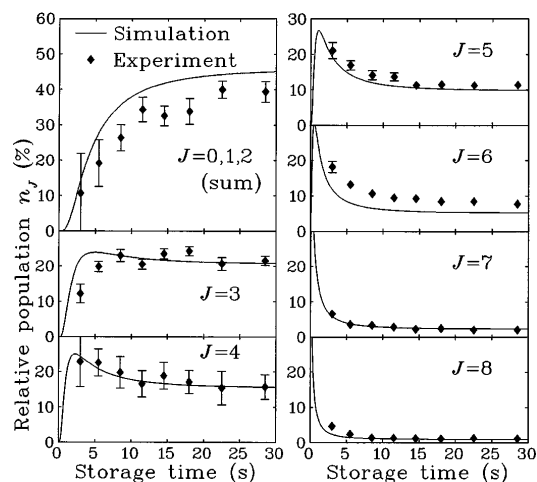


FIG. 3. Populations of low rotational levels $X^1\Sigma^+(v=0, J)$ as a function of storage time. For long storage, the distribution approaches room temperature (300 K).

[7], the populations can be estimated by a fit to the experimental spectrum. We used only the continuous parts of the data, the continua of the theoretical $\sigma_J(\bar{\nu})$ being less sensitive to the input potential curves than the resonant parts. As there are no flat parts between the groups $J=0, \dots, 2$, the corresponding populations n_0, \dots, n_2 could not be determined separately, but only their sum n_{012} . The highest monitored rotation was $J=8$.

The distributions thus determined clearly exhibit rotational cooling (Fig. 3, dots); as the storage time increases, the lowest levels $J=0, \dots, 3$ are fed, higher rotations are depleted. The final temperature is $T_f = 300_{-50}^{+50}$ K. We have modeled the relaxation assuming initially hot (≥ 1000 -K) CH^+ molecules in levels $X^1\Sigma^+(v=0, J=0, \dots, 8)$ decaying in a blackbody radiation field of 300 K (Einstein coefficients from Ref. [23]), yielding satisfactory agreement with experiment (Fig. 3, full lines). Apart from confirming the input Einstein coefficients, this shows that there is no significant collisional heating. For the worst-case assumption that collisional heating and radiative cooling powers cancel at a $T_f = 350$ K, our results suggest an upper limit of only $\approx 10 \text{ K s}^{-1}$ for the collisional heating rate of CH^+ . As long as radiative cooling is much faster, it will probably dominate for any infrared-active molecular ion beam under typical storage ring conditions.

In summary, we have shown that photofragment spectroscopy at a storage ring can yield spectra of cold molecular ions, with valuable information added by the storage time dependence of the spectra. Taking near-threshold photodissociation of CH^+ in low rotational states as a benchmark problem, we have observed the predicted resonances between the C^+ fine-structure states for the first time. Further analysis of the spectrum will considerably improve the knowledge of the CH^+ threshold region and perhaps justify a new calculation of the radiative associa-

tion rate. From the time dependence, it is now clear that the rotational distribution of the stored beam is dominated by radiative cooling and can reach room temperature. This result is important for many experiments performed with molecular ions in storage rings.

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