Electron affinity of CH

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We measured the thresholds for photodetachment from the first and second excited rotational levels of CH^- to the lowest vibrational, rotational, and fine-structure level of CH to be $E_1 = 1.213 \pm 0.002$ eV and $E_2 = 1.206 \pm 0.002$ eV, respectively. Based on these measurements and the rigid rotor approximation, we arrive at an electron affinity of $EA = E_1 + \frac{1}{2}(E_1 - E_2) = 1.217 \pm 0.002$ eV. This value deviates from earlier experimental results but agrees with the calculation by Feller [J. Chem. Phys. **144**, 014105 (2016)]. In the present experiment, we stored ensembles of initially hot CH^- in the cryogenic ion-beam storage ring Double ElectroStatic Ion-Ring ExpEriment (DESIREE) for tens of seconds such that the vast majority of the ions were in the few lowest excited rotational levels of the electronic and vibrational ground state. We identified the initial states for photodetachment channels with threshold energies E_1 and E_2 by comparing the time dependences of measured photodetachment signals with radiative rotational-cooling rates calculated using the literature values of the dipole moment of CH^-. The conditions of a few occupied rotational levels are superior to those of previous studies of this system and an important step toward future studies with an all-rotational-ground-state ion beam.

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I. INTRODUCTION

The electron affinity of CH was investigated in a number of previous studies. To our knowledge, the first one was performed by Feldmann, who studied photodetachment using a beam of CH^- ions [1]. An energy threshold for electron detachment at 0.74 ± 0.05 eV was then identified as the electron affinity of CH [1]. Two following studies by Kasdan *et al.* [2] and Goebbert [3], however, arrived at much higher values of 1.238 ± 0.008 and 1.26 ± 0.02 eV, respectively. Okumura *et al.* [4] stored CH^- in an ion trap at room temperature for about 5 s, aiming to measure the lifetime of the metastable $a^1\Delta$ state of CH^-. Furthermore, Okumura *et al.* set lower and upper bounds on the electron affinity of 1.16 and 1.68 eV, respectively [4]. These previous studies were all performed at room temperature and with ions occupying a large number of rovibrational levels. Hence, it was not possible to resolve the initial and final rotational levels of the investigated transitions. Here, we use the cryogenic ion-beam storage ring Double ElectroStatic Ion-Ring ExpEriment (DESIREE) at Stockholm University [5–8] to store beams of CH^- ions for several tens of seconds before measuring the photodetachment signal as a function of the photon energy with a tunable laser.

During storage in DESIREE, the ions relax to their vibrational ground state and first few excited rotational levels, as previously demonstrated for cryogenically stored beams of OH^- ions [8,9]. In photodetachment studies of OH^- in ion traps [10,11], the ions were cooled to the lowest few rotational levels of the electronic and vibrational ground state through interactions with a buffer gas, while in the storage ring experiments [8,9] they cool spontaneously via infrared emission. In addition to being important as proofs of principle for the storage and cooling of small molecular anions, these experiments were also used to extract information on the intrinsic lifetimes of the rotational levels and the dipole moment of OH^-. A few other molecular systems have been studied using similar methods, such as CH^+ [12,13], NH_2^- [14], CN^- [15], N_2O^+ [16], and C_2^- [17,18].

In a recent study at the DESIREE facility [5–8], the lifetime of the metastable electronically excited $a^1\Delta$ state of CH^- was measured to be 14.9 ± 0.5 s using a time-dependent photodetachment technique [19]. This lifetime is about a factor of 2.5 longer than previously measured [4] and calculated [20,21] values, demonstrating the importance of long-time storage capabilities for lifetime measurements. Here, we present near-threshold photodetachment spectroscopy for ensembles of CH^- ions stored as a beam in a cryogenic ion-beam storage ring and report electron detachment thresholds for the first and second rotationally excited levels. These levels dominate the population in the present ion-storage-time range of tens of seconds.

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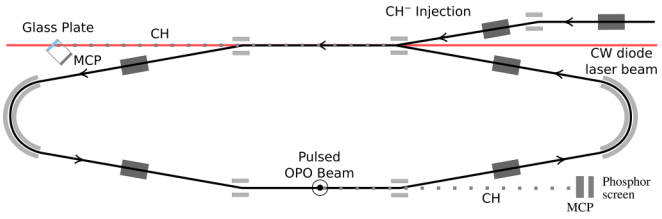


FIG. 1. Schematic of the ion-beam storage ring used in the experiment. A pulsed OPO is used for photodetachment in a perpendicular orientation, and the resulting neutral products are counted as functions of photon energy and time after ion injection using an MCP assembly with a phosphor-screen anode. On the other straight section of the ring, a diode laser is overlapped in parallel with the ion beam for normalization purposes (see text).

A direct measurement of the electron-affinity-defining threshold was not possible (under the present experimental conditions) due to the very small initial population of the $N = 0$ rotational ground state and the very long (>200 s) lifetime of the lowest rotationally excited ($N = 1$) state of CH^-. Instead, we deduce the electron affinity from the measured thresholds for the first and second excited rotational states according to the rigid rotor approximation, yielding the result $EA = E_1 + \frac{1}{2}(E_1 - E_2) = 1.217 \pm 0.002\,eV$. To ensure that the thresholds E_1 and E_2 were correctly assigned, we measured the time dependences of the photodetachment signal at three photon energies close to threshold and compared them with calculated lifetimes of the rotational levels.

II. EXPERIMENTAL SETUP AND METHOD

The DESIREE facility has been described in detail before [5,6], and the techniques to produce, store, cool, and photodetach CH^- were described in Ref. [19]. We used one of the cryogenic electrostatic ion-beam storage rings of the DESIREE facility (see Fig. 1) for the present experiment. The temperature of the storage ring is 13.5 ± 0.5 K, while OH^- ions stored in a previous experiment were found to approach an effective rotational temperature of 20.6 ± 0.5 K [8]. The CH^- beam is extracted from a cesium-sputter ion source using ethanol vapor. The ions are accelerated to 10 keV and are then mass selected using a bending magnet. After the magnet, the CH^- beam is transported to the storage ring, injected, and stored for up to 500 s with an average storage lifetime of 300 s [19]. Two light sources for photodetachment are used. The first one is a widely tunable pulsed optical parametric oscillator (OPO) laser system with a bandwidth of 5 cm^{-1} and a repetition rate of 10 Hz, aligned perpendicularly to the ion beam. Neutral CH molecules resulting from photodetachment by the OPO are detected by a triple-stack microchannel plate (MCP), in combination with a phosphor-screen anode and a photomultiplier tube [22]. The second laser system is a continuous-wave diode laser with a photon energy of 1.96 eV, which is far beyond the detachment threshold for any rovibrational level of the CH^- ion, and provides a photodetachment signal used for ion-beam current normalization. The diode laser is aligned in parallel with the ion beam along one of the straight sections of the ring, as shown in Fig. 1, and the resulting neutral CH molecules hit a glass plate covered by a single graphene layer. This plate transmits the laser light, but when hit by a neutral particle, it produces secondary electrons, which in turn are detected by an MCP detector [23].

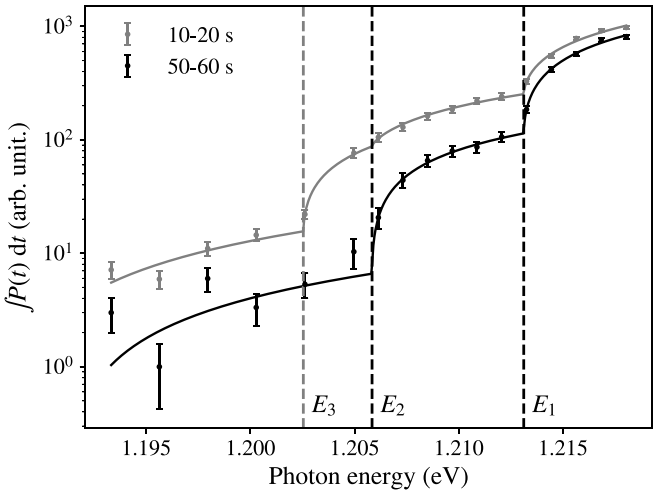


FIG. 2. Time-integrated photodetachment rates as a function of photon energy for 10–20-s storage (gray data points) and for 50–60-s storage (black data points). The vertical dashed lines are photodetachment thresholds extracted from fits to Eq. (1). Note the logarithmic vertical axis.

III. PHOTODETACHMENT THRESHOLD MEASUREMENTS

The task of measuring the electron affinity by scanning the photon energy over the threshold would be straightforward if all ions could be prepared in the lowest rovibrational level of the electronic ground-state potential. However, the lifetimes of the lowest excited rotational levels are very long, and the direct production of nonrotating molecular ions in the violent-sputtering ion-production process is highly unlikely. Therefore, we use the somewhat more elaborate scheme mentioned above. We experimentally establish the steep thresholds related to the *lowest* available state of the neutral CH molecule. They are the most visible increases in the photodetachment signal because they occur at photon energies where transitions from specific rotational states in CH^- to the lowest-energy state in CH first become possible and therefore correspond to large increases in the fractions of the ions in the stored beam that may be photodetached. By varying the time after injection at which we perform the photodetachment measurement, we can, to some extent, control the contributions from different CH^- rotational levels. However, the population of the rotational ground state remains small at all storage times in the present experiment.

Here, we measure the photodetachment signal within two different windows of time after ion-beam injection. The photon energy is scanned over a narrow range close to the expected thresholds by switching its setting at every injection. This scanning procedure is repeated a large number of times in order to average out any possible long-term changes in the beam current. In Fig. 2, we show the measured integrated photodetachment rate as a function of the photon energy between 1.193 and 1.218 eV. The gray data show the integrated signal

between 10 and 20 s of storage, and the black data show the corresponding signal between 50 and 60 s of storage. For the 50–60-s storage-time interval, two thresholds are observed at 1.206 and 1.213 eV, where the latter is the dominant feature in the data. To extract the threshold-energy values, we model the photodetachment signal $P(E)$ with the Wigner law [24]

$$P(E) = \sum_i c_i (E - E_i)^p + Ek + s, \tag{1}$$

where E is the photon energy and E_i is the ith threshold energy. The factor c_i is proportional to the population of the lower state in the transition with threshold E_i, the transition strength, and the laser intensity. The empirically determined exponent p is related to the threshold behavior of the photodetachment cross section (here determined to be $p = 0.63 \pm 0.09$), and k and s are constants used to model the observed background below the thresholds. Similar models of the photodetachment cross section were previously applied successfully for molecular ions (see, e.g., Refs. [8,9,15]). Equation (1) is fitted to the data for 50-60 s of storage to extract the two threshold energies indicated by the black vertical dashed lines in Fig. 2, yielding $E_1 = 1.213 \pm 0.002$ eV and $E_2 = 1.206 \pm 0.002$ eV. The gray data recorded during 10–20 s of storage indicate that another threshold is present below E_2. To extract this threshold, E_3, Eq. (1) is fitted to the gray data in Fig. 2 using three thresholds, where the values for E_1, E_2, and p from the fit to the black data are used. The resulting threshold is $E_3 = 1.203 \pm 0.002$ eV, which is indicated by the gray vertical dashed line in Fig. 2. Note that the uncertainties in the threshold energies are dominated by the accuracy of the calibration of the photon energies. The observed thresholds in Fig. 2 cannot be directly assigned by means of any previous CH^- studies. This is not surprising since all previous studies worked with hot ions occupying a large number of rovibrational levels with a much larger number of transitions. In the present experiment, after tens of seconds of storage, only the few lowest rotationally excited levels of the vibrational ground state are significantly populated.

IV. SCHEMATIC ENERGY-LEVEL STRUCTURES IN CH^- AND CH

The electronic ground state of CH^- has $^3\Sigma^-$ symmetry. The rotational energy levels are approximately given by the rigid rotor model: $E(N) = BN(N+1)$, where B is the rotational constant and N is the angular momentum of CH^-, excluding spin. Coupling to the spin ($S = 1$) results in fine-structure splittings into three levels for each value of $N \neq 0$ with total angular momenta, $J = N + 1$, N, and $N - 1$. Analytical expressions for the energy levels have been derived and utilized for several systems with $^3\Sigma^-$ symmetry, such as O_2 [25]. These expressions contain parameters for spin-spin interactions, which, like the parameters for spin-rotational couplings, are unknown for CH^-. However, for systems where the rotational constant B is relatively large, the fine-structure splittings are often negligible compared to the separation between the different N levels. One example of such a system is the NH molecule, which is isoelectronic to CH^-. For NH, the fine-structure splitting between $J = 1$ and $J = 2$ of the $N = 1$ level is only about 0.1 meV, while the splitting between

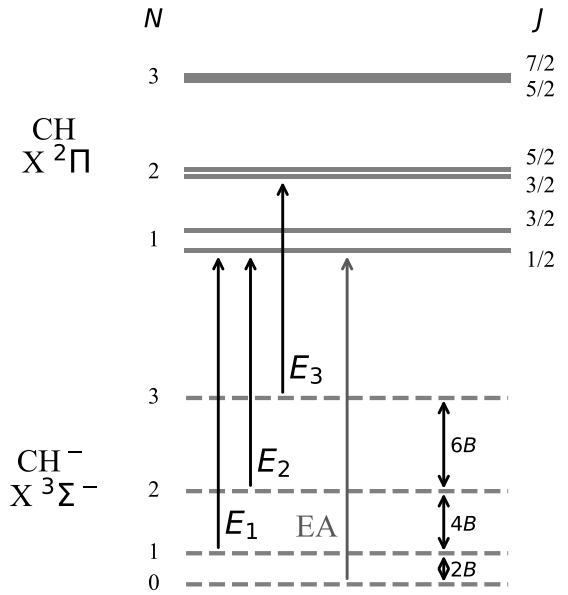


FIG. 3. Schematic of the ground and first excited rotational levels of the electronic ground states of CH^- (dashed lines) and CH (solid lines). Note that the absolute energy difference between the states of the ion and the states of the neutral is not to scale. The observed thresholds E_1, E_2, and E_3 are assigned to the indicated transitions. Details of the assignments are given in the text.

the first two rotational levels is 3.8 meV [26]. The rotational structure of *neutral* CH is well-known and has been calculated (see, e.g., Ref. [27]). The electronic ground state is $X^2\Pi$, and each N level is split into two J levels with $J = N + 1/2$ and $J = N - 1/2$. The separations of the J levels decrease with N, and for $N = 1$ the separation is 3.5 meV [27]. A schematic energy-level diagram of the rotational states of CH^- and CH is given in Fig. 3, where we have tentatively assumed that the E_1 and E_2 thresholds are the ones for detaching an electron from CH^- in the vibrational ground state and have rotational levels $N = 1$ and $N = 2$, forming the neutral CH in its lowest rovibrational and fine-structure level ($N = 1, J = 1/2$). From these thresholds and by assuming that the unknown fine-structure splittings within the $N = 1$ and $N = 2$ levels in CH^-, like the corresponding ones in NH [26], are negligibly small, we determine the electron affinity of CH to be $\mathrm{EA} = E_1 + 2B = E_1 + \frac{1}{2}(E_1 - E_2) = 1.217 \pm 0.002$ eV.

V. MEASURING AND MODELING THE TIME DEPENDENCE OF THE CH^- ROTATIONAL DISTRIBUTION IN THE STORED BEAM

To demonstrate that the tentative assignments of thresholds E_1 and E_2 are correct, we probe the time evolution of the rotational distribution in the stored CH^- beam. We select three photon energies: 1.218 eV, which should be beyond the electron affinity allowing photodetachment of CH^- ions in any quantum state; 1.214 eV, which should be above the threshold for detachment for all ions with $N \geqslant 1$; and 1.212 eV, which should allow detachment for only $N \geqslant 2$. We then measure the photodetachment yields as a function of storage time for these three photon energies. In addition, we apply the diode

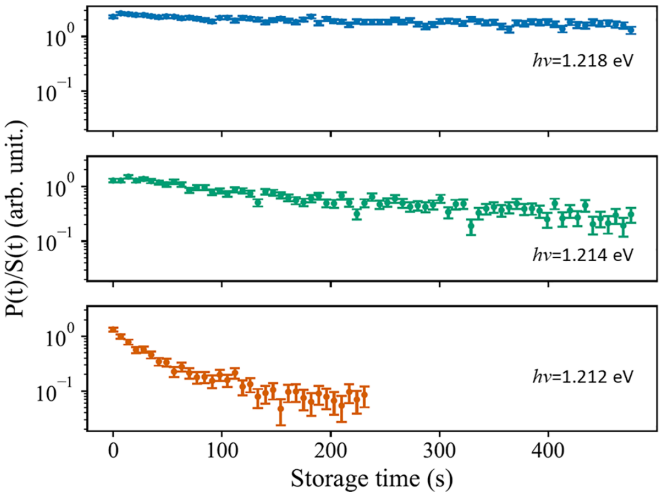


FIG. 4. Normalized photodetachment signals as a function of ion-beam storage time for three photon energies chosen such that all ions (blue points; 1.218 eV), all ions with $N \geqslant 1$ (green points; 1.214 eV), or all ions with $N \geqslant 2$ (orange points; 1.212 eV) may be photodetached. Note that the three vertical scales are not directly comparable for the blue, green, and orange datasets (see text).

laser with a photon energy of 1.96 eV, chosen high above the threshold in order to provide a photodetachment signal $S(t)$ for normalization, which is (nearly) independent of the N-level distribution of the stored CH^- beam. Through this procedure, $P(t)/S(t)$, where $P(t)$ is the photodetachment signal, should not be very sensitive to the overall decline in the ion-beam intensity as a function of storage time, t.

In Fig. 4, we show the measured normalized signals $P(t)/S(t)$ as a function of time t after injection for the three selected photon energies. For the measurement with the highest photon energy (1.218 eV), the normalized photodetachment signal varies slightly with time, although at this photon energy all ions can contribute to the signal at all times. We ascribe this slight decrease in the normalized signal to the decrease in average rotational excitation and thereby a decrease in the effectively rotational excitation averaged photodetachment cross section at 1.218 eV. At the lower photon energies of 1.214 and 1.212 eV, the photodetachment signals decay with time constants of hundreds and tens of seconds, respectively. Note that the higher $P(t)/S(t)$ values at short times for a photon energy of 1.218 eV (blue points, top panel of Fig. 4) compared to 1.214 eV (green points, middle panel Fig. 4) are *not* due to a substantial $N = 0$ population, but rather reflect a much higher photodetachment cross section at 1.218 eV than at 1.214 eV because the former energy is much higher above the E_1 threshold than the latter [see Eq. (1) and Fig. 2].

In order to relate these time dependences to the assignments of thresholds, we calculate the expected lifetimes of the rotational levels in the electronic and vibrational ground state of CH^- within the rigid-rotor approximation. The Einstein coefficient for the spontaneous decay from $N+1$ to N is given by [28]

$$A_{N+1\to N} = \frac{16\pi^3\nu^3\mu_0^2(N+1)}{3\epsilon_0 hc^3(2N+3)}, \tag{2}$$

where ν is the transition frequency, μ_0 is the dipole moment of CH^- calculated from its center of mass, ϵ_0 is the vacuum permittivity, h is Planck's constant, and c is the speed of light. There are at least two theoretical values of the dipole moment μ_0 of the ground state ($X^3\Sigma^-$) of CH^- reported in the literature [29,30]. These two results differ by less than 10%, and we use the most recent one, $\mu_0 = 1.29$ D [29]. (For the evaluation of Eq. (2), we converted the value from Ref. [29], which was given with reference to the position of the carbon nucleus, to the corresponding value with reference to the center of mass of CH^-). With this, we find that the theoretical lifetimes of the first few excited rotational levels of CH^- are 232, 24.2, and 6.68 s for $N = 1$, $N = 2$, and $N = 3$, respectively. With these approximate rotational-level lifetimes, our observation that the photodetachment signal decays with a decay time of tens of seconds for 1.212-eV photons and a decay time of hundreds of seconds for 1.214-eV photons shows that the threshold observed between these two photon energies, $E_1 = 1.213$ eV, is, indeed, the $N = 1$ threshold.

In order to investigate the influence of the initial distribution on the observed photodetachment signals after tens of seconds of storage, we model the time evolution of an initially hot rotational distribution—resulting from the ion production—toward equilibrium with the effective thermal radiation field inside DESIREE. The latter is assumed to follow Planck's law for blackbody radiation with an effective temperature of 21 K, as determined in a previous study of the relaxation of OH^- ions [8]. With the Einstein A coefficients given by Eq. (2)—and the related Einstein B coefficients—we calculate the rates for excitation and deexcitation and set up a system of linear first-order differential equations with an arbitrary number of N levels included. The solutions yield the relative population of the N levels as a function of storage time in the ring when the initial population distribution is specified. Due to the fact that higher rotational levels decay much faster, the populations at the timescales of the present experiment are not very sensitive to the initial conditions, and we demonstrate this—and make use of this fact—by tentatively assuming two very different initial population distributions given by Boltzmann distributions with effective rotational temperatures of 2000 and 10 000 K, respectively.

In Fig. 5, we show the results of this model calculation for populations of ions with $N \leqslant 1$, $N \leqslant 2$, and $N \leqslant 3$. Results are shown for both 2000 and 10 000 K initial temperatures, but no difference is visible, implying that for sufficiently highly excited initial rotational distributions the results in Fig. 5 should be valid for the timescales of tens of seconds relevant to the present experiment. The qualitatively similar time dependences of the data shown in orange ($N \geqslant 2$ in Fig. 5 and the photodetachment signal at 1.212 eV in Fig. 4) and of the data shown in green ($N \geqslant 1$ in Fig. 5 and the photodetachment signal at 1.214 eV in Fig. 4) once again underscore that the thresholds E_1 and E_2 are correctly assigned.

The threshold observed at 1.203 eV is less well established and is not included in our electron affinity determination. We assign it to a transition from $N = 3$ in CH^- to $N = 2$, $J = 3/2$ in CH. The measured thresholds and the deduced electron affinity are summarized in Table I, in which the 2-meV systematic uncertainty on the laser photon energy is the dominating source of error.

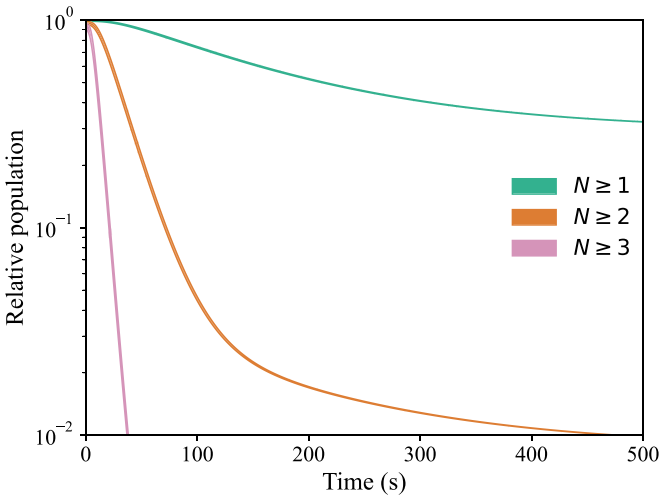


FIG. 5. Simulated fractional populations of groups of rotational states of CH^- with $N \geqslant 1$ (green curve), $N \geqslant 2$ (orange curve), and $N \geqslant 3$ (violet curve) for ensembles of CH^-. Initial population distributions with Boltzmann factors with temperature parameters of 2000 and 10 000 K yield indistinguishable results. The $N \geqslant 1$ (green) and $N \geqslant 2$ (orange) curves have the same qualitative time dependences as the equivalent datasets in Fig. 4.

TABLE I. Summary of the results of the present work.

Measured threshold	Value (eV)
E_1	1.213 ± 0.002
E_2	1.206 ± 0.002
E_3	1.203 ± 0.002
Electron affinity	Value (eV)
$\mathrm{EA} = E_1 + \frac{1}{2}(E_1 - E_2)$	1.217 ± 0.002

VI. SUMMARY, CONCLUSIONS, AND OUTLOOK

We used the cryogenic ion-beam storage ring DESIREE at Stockholm University in order to study photodetachment of CH^-. By storing the ions for tens of seconds or longer, they have time to cool radiatively, and measurements can be performed that involve very few quantum states. This opens up the possibility to perform measurements of photodetachment thresholds and electron affinities with higher precision than what is possible for room-temperature anions.

Here, we reported the energies for three transitions from the three lowest rotationally excited levels of the lowest vibrational state in the electronic ground state of CH^-. Our electron affinity value of $\mathrm{EA} = 1.217 \pm 0.002\,\mathrm{eV}$ is much more precise than—and differs significantly from—the most precise earlier measurements at $\mathrm{EA} = 1.238 \pm 0.008\,\mathrm{eV}$ [2] and $\mathrm{EA} = 1.26 \pm 0.02\,\mathrm{eV}$ [3]. Theoretical predictions of the electron affinity vary, but we note that the, to our knowledge, most recent calculation by Feller [31] yielded a value of 1.215 ± 0.001 eV, in agreement with the experimental value reported here.

Finally, we would like to mention that the already extremely low residual gas density (1–5 H_2 molecules/mm^3) and the very weak blackbody radiation field (characterized by an effective temperature of 21 K) in DESIREE are to be reduced even further in ongoing instrument-upgrade projects. It may thus—in the not too distant future—become possible to measure the threshold for photodetachment from the rotational ground state CH^- and thus the electron affinity of CH directly through a single threshold measurement. In addition, lasers could be used to remove all rotationally excited CH^- molecular anions from the stored beam to further improve the experimental conditions. However, even when such direct electron affinity measurements become possible in the case of CH and other molecules with similarly small moments of inertia (and therefore large rotational constants), most molecular ions will decay much slower, and indirect methods like the one described in the present work will still be required.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [32].

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