

Electron Affinity of the Carbon Dimer from Threshold Photodetachment Spectroscopy

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Photodetachment spectroscopy of C_2^- anions across the thresholds to the two lowest electronic states of neutral C_2 was carried out using rotationally cold trapped ions. The electron detachment was observed to follow p - and s -wave threshold behavior for transitions to the $C_2X^1\Sigma_g^+(v'=0)$ and $C_2a^3\Pi_u(v'=0)$ states, respectively, in agreement with the threshold laws derived by Wigner [Phys. Rev. **73**, 1002 (1948)]. The ions were prepared at two different rotational temperatures, using a temperature-variable cryogenic 16-pole wire trap at 8 and 142 K, respectively. By fitting the two thresholds, an accurate value of the adiabatic electron affinity of C_2 was determined as 26364.2 ± 0.5 cm⁻¹. The energy of the p -wave threshold was found to be particularly insensitive to rotational excitation, due to the absence of P - and R -branch excitations. The new electron affinity deviates significantly from a recent measurement using photoelectron spectroscopy [Laws *et al.* Nat. Commun. **10**, 5199 (2019)].

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The carbon dimer, C_2 , is a widely studied molecular species. It is an abundant intermediate in combustion or in electric discharges involving hydrocarbons. Its electronic structure is of open-shell character, which makes C_2 highly reactive and provides it with many low-lying electronic states. These states have been studied spectroscopically for almost two centuries [1], starting with the characteristic Swan bands first described in 1802 [2]. C_2 absorption and emission spectra are also observed in a variety of astrophysical environments, including the interstellar medium [3,4], the Red Rectangle protoplanetary nebula [5–8], comets [9–11], and stars [12,13] such as the Sun [14]. For *ab initio* calculations, C_2 is an important benchmark system, as its multireference character makes it a particularly challenging molecule to calculate [15].

The negative ion of the carbon dimer, C_2^- , is one of the most widely studied molecular anions. Unlike most negative molecular ions, it possesses excited electronic states below the lowest photodetachment threshold and is therefore amenable to optical spectroscopy. After its first observation [16], the first high resolution measurement was carried out more than 50 years ago [17]. Many more experiments followed, see, e.g., Refs. [18–23]. Recently,

also inner-shell photoexcitation [24] and autodetachment out of metastable quartet states [25] of C_2^- were investigated. Many *ab initio* calculations have focused on C_2^- , making it an important benchmark system for theory (see, e.g., Refs. [15,26–30]). Based on the available electronic states, C_2^- has been proposed as a promising candidate for direct Doppler laser cooling [31]. Using vibrational quenching collisions to close the photon cycle, fluorescence detection of a cloud of trapped C_2^- was achieved [32].

C_2^- anions are speculated to exist in the interstellar medium, where several polar negative ions have been detected, see, e.g., Refs. [33,34], but due to the absence of dipole-allowed rotational or rovibrational transitions, no direct observation has been achieved so far. A search in the visible spectrum of a hydrogen-deficient carbon star found no signatures of C_2^- , which led to the conclusion that photodetachment may be a prominent destruction pathway for interstellar C_2^- [35].

The adiabatic electron affinity of C_2 , the energy difference between the ground states of C_2 and C_2^- , is a benchmark quantity of the electronic structure of both species [36]. Electron photodetachment measurements of C_2^- in the optical range revealed sharp resonances that were attributed to autodetachment from higher vibrational states of the anion [37]. Accurate values of the adiabatic electron affinity of C_2 were later obtained by photoelectron spectroscopy [38], and more recently refined using photoelectron imaging of C_2^- [39]. However, the recent experimental value disagrees with accurate quantum calculations [36].

In this letter, we present a new and more accurate value of the adiabatic electron affinity of C_2 obtained using direct

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photodetachment spectroscopy, a fundamentally different method from previous investigations of C_2^- . This technique has been employed previously to measure electron affinities [40], to detect dipole-bound states close to threshold [41–44], to probe the long-range interaction of the outgoing electron [45], and to determine anion rotational state populations [46–50]. Here, we carried out photodetachment measurements across the $C_2X^1\Sigma_g^+(v'=0) \leftarrow C_2^-X^2\Sigma_g^+(v''=0)$ and $C_2a^3\Pi_u(v'=0) \leftarrow C_2^-X^2\Sigma_g^+(v''=0)$ thresholds using trapped ions in a cryogenic 16-pole wire trap. The experiment was performed at two different temperatures, which allowed us to vary the rotational-state distribution of the $C_2^-X^2\Sigma_g^+(v''=0)$ ground state. The near-threshold cross sections are modeled using the Wigner threshold law [51] including relative rotational line intensities [52,53]. With recent improvements of the stability of the trapped ion signal, we are able to show the p -wave behavior of photodetachment to $C_2X^1\Sigma_g^+(v'=0)$, despite the very small detachment cross section near threshold. In contrast, photodetachment to $C_2a^3\Pi_u(v'=0)$ follows s -wave behavior. These results imply that photodetachment predominantly occurs out of s - and p -like orbitals, respectively, in agreement with findings from previous photoelectron imaging studies [39]. However, our value of the adiabatic electron affinity of C_2 differs significantly from the value reported in that work. The results demonstrate that reliable spectroscopic constants can be obtained from photodetachment data at a p -wave threshold, despite the slow increase of the cross section in this region.

A detailed description of the experimental setup is provided elsewhere [23,54]. Dicarbon anions are produced in a plasma discharge in a supersonic expansion of a gas mixture containing 5% acetylene, 5% carbon dioxide, and 90% argon. A set of Wiley-McLaren-style electrodes are used to accelerate the ions toward a quadrupole bender, which deflects them by 90° toward the ion trap. Time-of-flight (TOF) mass separation allows for the mass-selective loading of the trap. The trap consists of 16 copper wires of 100 μm diameter that function as radiofrequency electrodes and confine the ions radially. The axial confinement is provided by hollow cylindrical end-cap electrodes, which are individually turned off and on to load and unload the trap. The trap setup is mounted on a closed-cycle cryostat, which was used to cool the trap to 8 K. For measurements at 142 K, heating elements were used to increase the trap temperature. After mass-selectively loading the ions into the trap, helium buffer gas, which is precooled to the trap temperature, is used to thermalize the trapped ions. Previous measurements of the rotational state populations have confirmed that the rotational temperature of the ions closely follows that of the buffer gas temperature [23]. Ultraviolet radiation from a frequency-doubled dye laser (Radiant Dyes, Narrow Scan, 0.06 cm^{-1} measured line-width) pumped by a frequency-doubled Nd:YAG laser

(100 Hz repetition rate) is then allowed to interact with the trapped ions for a specific exposure time. Photodetachment leads to a single exponential decrease of the number of trapped ions; the remaining ions are released from the trap and detected on a microchannel plate (MCP) detector after TOF mass separation. The mass-resolving power of 46 is high enough to clearly distinguish C_2^- from C_2H^- , which is also created in the source and trapped in small quantities.

For accurate determination of the photon wave number, a small portion of the fundamental output of the dye laser is guided to a wave meter (HighFinesse WS-7, 0.002 cm^{-1} accuracy), which is calibrated to a Doppler-free rubidium absorption line (see Supplemental Material [55]). To normalize to photon flux, the laser power is measured on a bolometer at the beam exit out of the vacuum chamber. The laser is guided through the trap in the axial direction, and the laser-ion interaction time is controlled by a mechanical shutter. For each laser frequency, the remaining ion signal is measured after one long and one short laser interaction time. The relative photodetachment cross section σ_{rel} is calculated as

$$\sigma_{\text{rel}} = \frac{\ln\left(\frac{[C_2^-]_{t_1}}{[C_2^-]_{t_2}}\right)}{\Phi(t_2 - t_1)}. \quad (1)$$

Here, $[C_2^-]_{t_1}$ and $[C_2^-]_{t_2}$ represent the ion signals measured on the MCP at short and long laser interaction times, respectively, and Φ is the relative photon flux at the location of the ions. A more detailed description of how we derive the cross section is given in the Supplemental Material [55]. The laser powers and the interaction times were adjusted across the measurement in order to keep the ion depletion in the range of 20%–70%. This experimental procedure is repeated across the scan range to obtain the relative photodetachment cross section as a function of photon wave number.

Figure 1 shows the combined photodetachment spectra obtained in this Letter. The relative photodetachment cross section shows a gradual increase as a function of photon wave number followed by a sharp rise, clearly revealing two photodetachment thresholds of different character. For nonpolar molecular ions, such as C_2^- , the threshold behavior of the photodetachment cross section σ_{pd} is described by the Wigner threshold law [51,61]

$$\sigma_{\text{pd}} \propto k^{2l+1}, \quad (2)$$

where k is the magnitude of the linear momentum of the ejected photoelectron and l represents the orbital angular momentum of the ejected photoelectron. To model the photodetachment cross section, we combine Wigner's law with an orbital ionization model, which assumes that the photon angular momentum is fully transferred to the

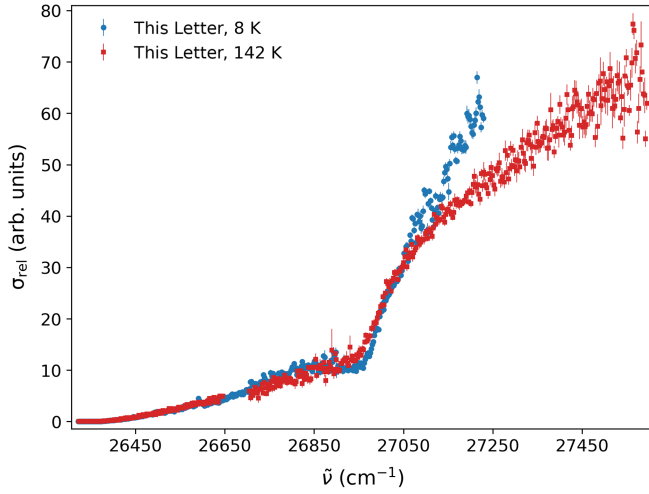


FIG. 1. Overview of the photodetachment spectra across the $C_2X^1\Sigma_g^+(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ and $C_2a^3\Pi_u(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ thresholds at 8 K (blue markers) and at 142 K (red markers).

photoelectron [52]. The photodetachment cross section is then expressed as

$$\sigma_{pd} = A \sum_{J'', T} P(J'', T) \times \left[\tilde{\nu} - \frac{E_{th}(J'', J')}{hc} \right]^{l+\frac{1}{2}} \times \theta \left(\tilde{\nu} - \frac{E_{th}(J'', J')}{hc} \right) \sum_{l''} \frac{1}{2l''+1} Q(l'', J'', J') a(l''), \quad (3)$$

where $P(J'', T)$ is a Boltzmann factor for the temperature-dependent population of rotational level $J'' = N'' \pm 1/2$ in the $C_2X^2\Sigma_g^+(v''=0)$ state. $\tilde{\nu}$ is the photon wave number and $E_{th}(J'', J')$ describes the energy difference between the corresponding rovibronic states of the anion and the neutral molecule, which includes the adiabatic electron affinity. A is an overall scaling factor. The Heaviside function θ removes transitions below the individual threshold energies. $Q(l'', J'', J')$ is the Hönl-London factor [52,53] (see Supplemental Material [55]) and $a(l'')$ is an l'' -dependent factor associated with the orbital angular momentum quantum number of the bound electron prior to detachment, l'' , arising from the leading term(s) of the central-field expansion of the molecular orbital [see Eq. (23) of Ref. [52]]. Only vibrationless transitions are included in the fit function, since the energy of $C_2X^1\Sigma_g^+(v'=1)$ lies above that of $C_2a^3\Pi_u(v'=0)$, outside the studied spectral region.

Since C_2^- and C_2 are homonuclear diatomic molecules without nuclear spin, various rotational levels are missing due to permutation symmetry. In the $C_2X^2\Sigma_g^+$ and $C_2X^1\Sigma_g^+$ states, only rotational states with even N'' are populated. In the $C_2a^3\Pi_u$ state, only odd levels of N' are allowed (see

Ref. [62]). At 8 K, only the three lowest rotational levels ($N'' = 0, J'' = 1/2$ and $N'' = 2, J'' = 3/2$ and $J'' = 5/2$) are populated significantly, whereas levels up to $N'' = 16$ contribute at 142 K (see Supplemental Material [55]).

The selection rule $l - l'' = \pm 1$ [63] for electron detachment implies that s -wave photodetachment ($l = 0$) necessarily arises from a p -like orbital in the anion ($l'' = 1$). For C_2^- this is not allowed for detachment to the C_2 ground electronic state as the molecular orbital from which the electron is ejected has gerade symmetry. p -wave photodetachment ($l = 1$) must originate from an s - or d -like electronic orbital, or from a linear combination of both. For the $C_2X^1\Sigma_g^+(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ photodetachment spectra shown by blue and red markers in Fig. 2 for two different trap temperatures, the slow rise in threshold behavior indicates that the ejected photoelectron has indeed predominantly p -wave character. Accordingly, we considered contributions from both s - and d -like orbital character to the photodetachment process, which restricts the rotational transitions to $\Delta N = 0, \pm 2$ (Q -, O -, and S -branch transitions, see Supplemental Material [55]). For the $C_2a^3\Pi_u(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ photodetachment spectra displayed in Fig. 3, the threshold behavior instead reveals predominantly s -wave character, i.e., photodetachment from a p -like orbital.

The photodetachment spectra of the $C_2X^1\Sigma_g^+(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ transition in Fig. 2 at 8 and 142 K were fitted using Eq. (3), with $a(0) = 1$, while $a(2)$, A and the adiabatic electron affinity were treated as fit parameters.

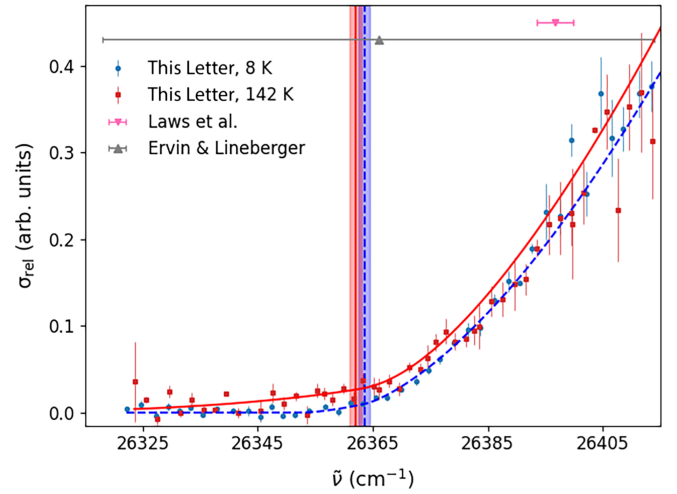


FIG. 2. Close-up views of the photodetachment spectra across the $C_2X^1\Sigma_g^+(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ threshold at 8 K (blue markers) and 142 K (red markers), together with fit curves based on Eq. (3) in the same colors. The adiabatic electron affinities extracted from the fits are indicated by vertical lines (blue dashed line for 8 K, red solid line for 142 K). For comparison, previously reported values from Laws *et al.* [39] and from Ervin and Lineberger [38] are included as pink and gray markers, respectively, at the top of the graph.

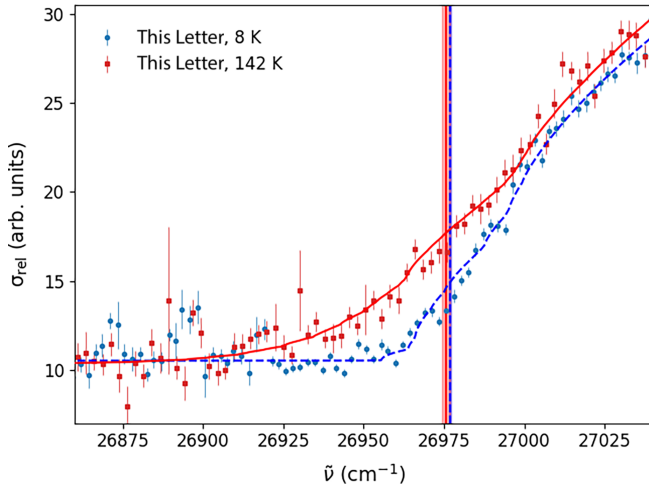


FIG. 3. Close-up views of the photodetachment spectra across the $C_2a^3\Pi_u(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ threshold at 8 K (blue markers) and 142 K (red markers), together with fit curves based on Eq. (3) in the same colors. Vertical lines (blue dashed line for 8 K, red solid line for 142 K) indicate the sum of the fitted adiabatic electron affinity and the difference between the vibronic term energies for $C_2X^1\Sigma_g^+(v'=0)$ and $C_2a^3\Pi_u(v'=0)$ of $612.120(4) \text{ cm}^{-1}$ (see main text).

The rotational level populations were calculated for the given temperatures, as discussed above. The resulting fit curves closely reproduce the experimental spectra. The vertical blue and red lines mark the adiabatic electron affinities obtained for the two temperatures. For the measurement at 142 K, the finite cross sections observed at photon wave numbers below the adiabatic electron affinity confirm contributions from O -branch transitions, which arise from the d -orbital character of the orbital out of which photodetachment occurs. The relative contributions of s - and d -orbital character are reflected in the parameters $a(0) = 1$ and $a(2) = 0.23(3)$, respectively. Excluding O - and S -branch transitions in the data analysis barely changes the fitted adiabatic electron affinities at 8 K, but shifts the adiabatic electron affinity at 142 K (see Supplemental Material [55]).

In the fits to the photodetachment spectra of the $C_2a^3\Pi_u(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ transition (Fig. 3) at 8 and 142 K, only an s -wave contribution ($a(1) = 1$) was included, with $E_{\text{th}}(J'', J')$, A and a vertical offset chosen as free parameters. Again, the fit curves are in very good agreement with the experimental spectra. Comparison of the 8 and 142 K data shows that the spectral onset shifts to lower wave numbers at higher temperature, which reflects the increased rotational excitation, similar to previous observations for OH^- [46] and CN^- [40]. Using the difference of the vibronic term energies for the $C_2X^1\Sigma_g^+(v'=0)$ and $C_2a^3\Pi_u(v'=0)$ states, calculated from known molecular constants to be $612.120(4) \text{ cm}^{-1}$ [62,64] (and tabulated in Ref. [38]), complementary values for the adiabatic electron affinities were obtained by

TABLE I. Adiabatic electron affinity (EA) values determined at two ion trap temperatures T as part of this Letter. EA_X and EA_a correspond to results from fits to the $C_2X^1\Sigma_g^+(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ and $C_2a^3\Pi_u(v'=0) \leftarrow C_2X^2\Sigma_g^+(v''=0)$ transitions, respectively. $\overline{\text{EA}}$ is the weighted average of these values. The given uncertainties are statistical.

T (K)	$\text{EA}_X(\text{cm}^{-1})$	$\text{EA}_a(\text{cm}^{-1})$	$\overline{\text{EA}}(\text{cm}^{-1})$
8	26363.5 ± 1.0	26364.7 ± 0.4	26364.2 ± 0.5
142	26362.1 ± 1.0	26363.3 ± 1.4	

subtracting this difference from the fitted threshold energies.

Table I provides a summary of the adiabatic electron affinities obtained from the four independent determinations described above, along with the weighted average value of $26364.2 \pm 0.5 \text{ cm}^{-1}$. Systematic uncertainties arising from the determination of the rotational temperature and the wave number calibration are considered to be negligible compared to the statistical uncertainties of the fits.

Table II presents a comparison of the determined adiabatic electron affinity of C_2 to values from previous photoelectron spectroscopic studies [38,39] and quantum calculations [36]. In the previous experimental studies, mass-selected beams of anions were intersected with fixed-frequency lasers far above threshold, and the kinetic energies of the ejected photoelectrons were measured and analyzed. In contrast to that, we employed a fundamentally different technique, in which a tunable photon source was used to measure the relative photodetachment cross section at the thresholds of two photodetachment transitions of cold C_2^- in a radiofrequency multipole ion trap. This technique only requires a calibrated laser, not a calibrated photoelectron spectrometer, which can be obtained with higher accuracy and reliability. The comparison shows that our new value for the adiabatic electron affinity of C_2 has greatly reduced uncertainties and differs significantly from the recent experimental value reported in Ref. [39]. Both of these values are compatible with the earlier determination by Ervin and Lineberger [38]. The present value also agrees well with the high level quantum calculation Ref. [36].

Our results confirm previous findings that electron detachment from $C_2^-X^2\Sigma_g^+$ occurs predominantly from s -like (corresponding to $3\sigma_g$) and p -like (corresponding to $1\pi_u$) orbitals for transitions into the ground $X^1\Sigma_g^+$ and

TABLE II. Adiabatic electron affinities of C_2 determined in this Letter and reported in earlier studies, in units of cm^{-1} .

Exp. [38]	Exp. [39]	Calc. [36]	This Letter
26366 ± 48	26396 ± 3	26350 ± 16	26364.2 ± 0.5

excited $a^3\Pi_u$ electronic states of C_2 , respectively [39]. For detachment into $C_2X^1\Sigma_g^+$, our data also indicate a non-negligible d -type character of the parent anion's molecular orbital from which photodetachment occurs. These results demonstrate the power of threshold photodetachment spectroscopy for probing intrinsic molecular structure and for obtaining accurate electron binding energies for a range of anionic systems, even when s -wave detachment is absent. They provide a high-accuracy benchmark for quantum chemical calculations and are expected to stimulate further high-level electronic-structure studies of C_2^- , their neutral counterparts and of related species. Potential future laser cooling [31] will make C_2^- an ideal system for further precision measurements.

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Data availability—The data that support the findings of this article are openly available [65].

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