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## Revision of the ionization energy of neutral carbon

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## PAPER

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**Abstract**

This publication describes a re-analysis of previously published data on neutral carbon (C I). We used critically examined and improved values for the line energies of the absorption spectrum of molecular iodine to calibrate the transition energies of C I absorption lines originating from the  $1s^2 2s^2 2p 3s^3 P^{\circ}_2$  level and terminating on highly excited Rydberg states of the  $1s^2 2s^2 2p n p^3 D_3$  series. This series converges on the first excited fine-structure level of the ionic ground configuration. Additional use of improved energy values for the  $1s^2 2s^2 2p 3s^3 P^{\circ}_2$  level and for the fine-structure interval of the ionic ground state together with modern fitting techniques lead to a new value of the ionization energy of neutral carbon with 9 times the precision of previous work,  $90\,820.348(9)\text{ cm}^{-1}$  (equivalent to  $11.260\,2880(11)\text{ eV}$ ), as well as a table of predicted values for the energies of unobserved states in the series.

**1. Introduction**

Accurate and precise values of photophysical quantities of atoms and molecules are important as input data in a number of fields, especially astrophysical calculations of properties, such as opacities, and chemical kinetics. These properties of the species involved include transition energies of both allowed and forbidden transitions, transition probabilities, dissociation energies of molecules, and ionization energies of the neutral and ionic species. A detailed review of the scope and importance of accurate photophysical data on carbon can be found in a recent paper by two of us [1].

Atomic carbon is a particularly important species in organic chemistry and astrophysics. In this brief article we describe a new determination of the ionization energy of neutral atomic carbon, based on the recent work [1] and a related re-evaluation of data previously published by one of us [2].

A number of previous studies have yielded ionization energy values with varying precision [3–5]. As measurement technologies have become more refined, it is the norm for measured atomic properties to become more accurate over time. A common precise method of determining ionization energies is to measure the energies above the ground state for a large number of members of one or more Rydberg series of the species of interest. Preferably, the series used should be free of perturbations, eliminating the need for a multichannel quantum defect theory treatment of the data. The evolution of laser spectroscopic techniques, along with improved values of atlases of calibration lines [6–8] (in this case the absorption lines of molecular iodine) has made new measurements possible, and also enabled the re-evaluation of older data to a higher degree of precision.

**2. Discussion of previously published results**

In our 1998 work [2], we used nanosecond pulsed VUV + UV two-photon resonant excitation to produce spectra of C I Rydberg atoms from  $[\text{Be}]2p^2\ ^3P_0$  ground state atoms prepared by laser ablation (henceforth, we omit the filled shells of the Be-like core  $1s^2 2s^2$  from the level designations in the text). That experiment utilized VUV resonance through selected fine structure levels of the  $2p 3s^3 P^{\circ}_j$  term (see the scheme of relevant energy levels and transitions in figure 1) followed by single-photon Rydberg state excitation.

This second-step excitation was made with wavelength-tunable UV light from a frequency-doubled probe dye laser, which was energy-calibrated at the fundamental wavelength of the probe laser by comparison to a

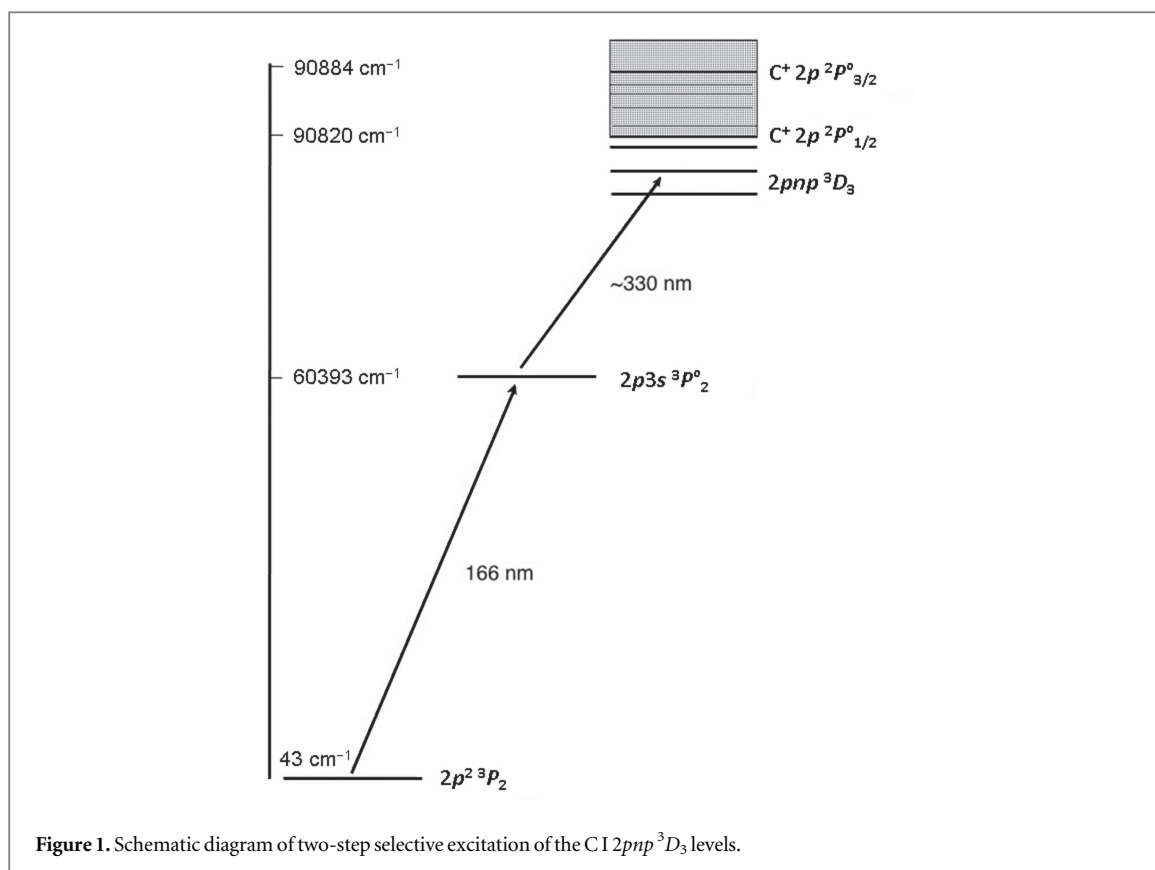


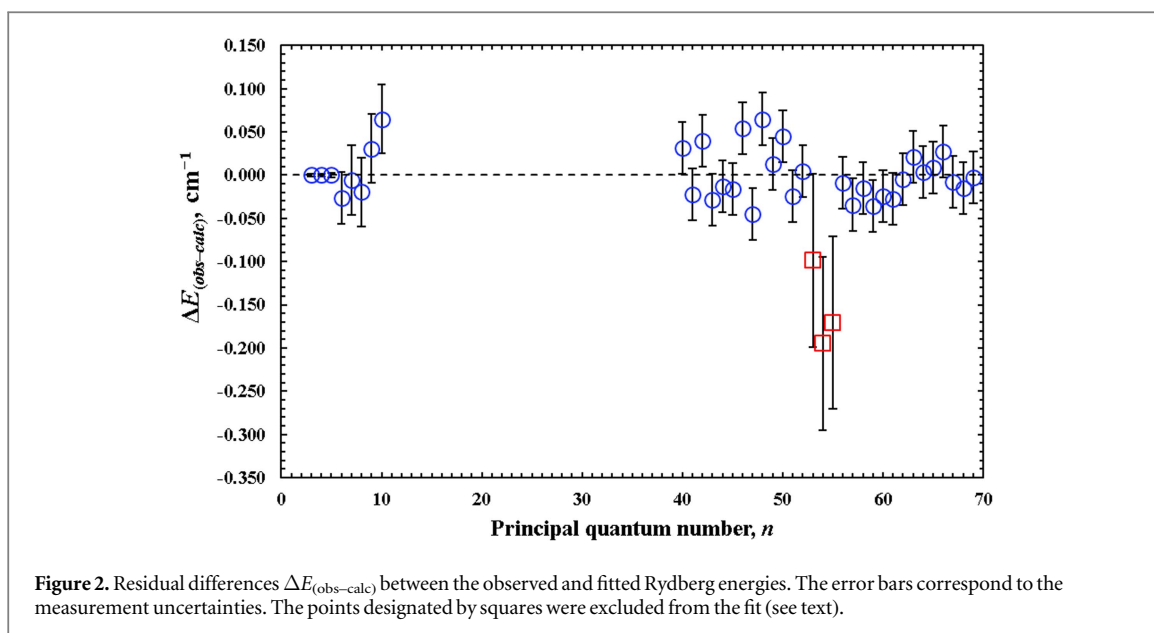
Figure 1. Schematic diagram of two-step selective excitation of the CI  $2pnp\ ^3D_3$  levels.

simultaneously recorded spectrum of ground state molecular iodine. This scheme produced excitation selective in the total angular momentum  $J$  of various Rydberg series converging to the  $^2P^{\circ}_{1/2}$  and  $^2P^{\circ}_{3/2}$  fine structure levels of the ground configuration  $2p$  of the  $C^+$  ion. Detection of the excited atoms was accomplished by collecting ions produced through either pulsed electric field ionization or autoionization. The ionization potential was determined through the use of the unperturbed  $2pnp\ ^3D_3$  series, which converges to the first excited ionic fine-structure level  $^2P^{\circ}_{3/2}$ . A simple fit of the observed transition energies to a Rydberg formula with a constant quantum defect gave an interval between the intermediate state and the  $^2P^{\circ}_{3/2}$  series limit of  $30\,490.54(3)\text{ cm}^{-1}$  with a quantum defect of  $0.673(10)$ . Added to the best available (at the time of the original work [2]) value of the intermediate  $2p3s\ ^3P_2$  level energy [5],  $60\,393.14(5)\text{ cm}^{-1}$ , the energy required to ionize the ground state atom to an ion in the excited  $^2P^{\circ}_{3/2}$  state was found to be  $90\,883.68(8)\text{ cm}^{-1}$ . At our level of precision, subtracting the value of the  $^2P^{\circ}_{1/2}-^2P^{\circ}_{3/2}$  energy splitting of the ionic ground configuration determined from far IR laser magnetic resonance [9],  $63.35\text{ cm}^{-1}$ , from our result for the  $^2P^{\circ}_{3/2}$  series limit did not increase the uncertainty and yielded a value of  $90\,820.33(8)\text{ cm}^{-1}$  for the first ionization limit of CI. This was in reasonable agreement with the result of [5], but slightly more precise.

### 3. Limitations of the accuracy of our previous result for the ionization energy

It should be noted that the precision of our result for the ionization energy could be improved in several ways. First, the major part of our uncertainty came from the value of the energy of the intermediate  $2p3s\ ^3P_2$  level. Since the time of our work, improved values for the resonance line energies have become available, making a correction possible. Additionally, two of us [1] derived accurate values for low  $2pnp\ ^3D_3$  levels for  $n$  between 3 and 10. Including these levels in the fit would be expected to yield an improved series limit energy.

There are also several developments that allow us to improve the accuracy of our observed Rydberg state energies. Our original photon energy calibration was performed utilizing absorption lines energies of iodine from the atlas of Gerstenkorn and Luc [10]. Since our earlier work, re-examination of the iodine spectrum [6–8] has shown that a weakly energy-dependent systematic correction factor ( $\approx -0.006\text{ cm}^{-1}$  at the probe laser frequencies in our spectral region) must be applied to the energies of Gerstenkorn and Luc. We derived additional corrections to the assumed energies of the observed iodine lines used for our calibration by convolving our experimental probe laser bandwidth with these improved values of the iodine lines to take account of blended lines and hyperfine structure. While providing improved energies for many lines, this work also determined that some blended lines were unsuitable for calibration at our level of resolution; therefore, these lines were not used in the process of re-calibrating our Rydberg wavenumbers.



**Figure 2.** Residual differences  $\Delta E_{(\text{obs-calc})}$  between the observed and fitted Rydberg energies. The error bars correspond to the measurement uncertainties. The points designated by squares were excluded from the fit (see text).

The scan rate that we used in our previous work was such that each iodine line had only 5 to 7 data points on it. This, combined with our noise level, made fitting of a Gaussian lineshape to each line to determine its center no more, or perhaps even less, accurate than ‘eyeball’ weighting the data points of the lines to determine their centers. Random errors introduced by using the visual technique are expected to average out in the determination of the energies of a large number of Rydberg states.

A further difficulty that we discovered later was that our linear actuator driving the grating of the probe dye laser (a Thorlabs<sup>4</sup> piezoelectrically driven micrometer) would occasionally behave non-smoothly, so that the energy scan rate in small regions of the spectrum (over a range of several wavenumbers) would significantly deviate from its nominal value. Since we calibrated the spectrum in pieces by using the iodine lines in a number of regions of about  $20 \text{ cm}^{-1}$  width each, fitting the observed iodine energies over each region to a polynomial function (generally second order), this led to relatively inaccurate values for a few of the carbon Rydberg lines.

#### 4. Recalibration of the Rydberg wavenumbers for the $^3D_3$ series and redetermination of the ionization energy

Due especially to the scan rate problem noted above, it was decided to recalibrate the Rydberg transition energies on an individual basis, using two or three iodine lines bracketing each carbon line and a linear fit of the iodine line energies to data point numbers (data were acquired in equal-energy steps, so their sequential numbers provided a linear energy scale) to determine transition energies for each principal quantum number  $n$ . These fits yielded revised Rydberg state transition energies; additionally, each fit gave a scan rate that could be used to verify the choice of iodine lines and identify the regions where scan rate disruptions occurred. We avoided the iodine lines that were deemed unreliable in the calibration. The uncertainties in the Rydberg state energies counted from the  $2p3s^3P^o_2$  level, as derived from these fits, were estimated to be approximately  $\pm 0.03 \text{ cm}^{-1}$  in the full double-frequency photon energy. This estimate was based on the standard deviation of our measured wavenumbers from the fit of the four-term modified Ritz formula [11, 12]:

$$\delta_n = c_0 + c_1/(n - c_0)^2 + c_2/(n - c_0)^4 + c_3/(n - c_0)^6, \quad (1)$$

where  $c_i$  are fitted constants and  $\delta_n$  is the quantum defect describing an empirical correction to the principal quantum number  $n$  required to satisfy the hydrogenic formula:

$$E_1 - E_n = RZ^2/(n - \delta_n)^2, \quad (2)$$

where  $E_1$  is the ionization energy,  $Z$  is the charge of the ionic core, and  $R$  is the mass-corrected Rydberg constant (for CI,  $R = 109\,732.299\,04 \text{ cm}^{-1}$ ).

We utilized all the available data ( $n = 3$  to  $10$  from [1] and our present results for  $n = 40$  to  $69$ ) in a four-term modified Ritz formula using the RITZPL [11, 12] code to perform a fit yielding the series limit energy with its associated uncertainty. The residuals of this fit are shown in figure 2 below.

<sup>4</sup> Commercial products are identified in this article for adequate specification of the experimental procedure. This identification does not imply recommendation or endorsement by NIST.

**Table 1.** Observed and Predicted Energy Levels of the [Be]2pnp  $^3D_3$  ( $n = 3$  to 69) series of neutral carbon.

$n$	$E_{\text{obs}}^a$ (cm $^{-1}$ )	$E_{\text{calc}}^a$ (cm $^{-1}$ )	$\Delta E_{(\text{obs}-\text{calc})}$ (cm $^{-1}$ )	$\delta_{\text{calc}}^a$
3	69 744.0521(13)	69 744.0521(13)	0.0000	0.721 663 250(22)
4	80 834.6249(13)	80 834.6249(13)	-0.0000	0.695 519 06(5)
5	84 985.0033(24)	84 985.0032(24)	0.0001	0.686 919 15(14)
6	87 002.31(3)	87 002.337(17)	-0.027	0.682 9267(15)
7	88 135.84(4)	88 135.846(20)	-0.006	0.680 7295(25)
8	88 836.15(4)	88 836.170(18)	-0.020	0.679 387(3)
9	89 299.13(4)	89 299.099(15)	0.031	0.678 505(3)
10	89 621.09(4)	89 621.025(13)	0.065	0.677 895(4)
11		89 853.925(11)		0.677 455(4)
12		90 027.847(10)		0.677 127(4)
13		90 161.152(9)		0.676 876(4)
14		90 265.571(9)		0.676 679(5)
15		90 348.887(8)		0.676 523(5)
16		90 416.425(8)		0.676 396(6)
17		90 471.934(8)		0.676 292(7)
18		90 518.108(8)		0.676 205(8)
19		90 556.930(8)		0.676 132(8)
20		90 589.881(8)		0.676 071(9)
21		90 618.089(8)		0.676 018(10)
22		90 642.422(8)		0.675 972(11)
23		90 663.558(8)		0.675 933(12)
24		90 682.035(8)		0.675 898(14)
25		90 698.279(8)		0.675 868(15)
26		90 712.638(8)		0.675 841(16)
27		90 725.391(8)		0.675 817(17)
28		90 736.770(8)		0.675 796(19)
29		90 746.965(8)		0.675 777(20)
30		90 756.135(8)		0.675 759(22)
31		90 764.412(8)		0.675 744(23)
32		90 771.910(8)		0.675 730(25)
33		90 778.722(8)		0.675 72(3)
34		90 784.931(8)		0.675 71(3)
35		90 790.605(8)		0.675 69(3)
36		90 795.803(8)		0.675 69(3)
37		90 800.579(8)		0.675 68(3)

Table 1. (Continued.)

$n$	$E_{\text{obs}}^a$ (cm $^{-1}$ )	$E_{\text{calc}}^a$ (cm $^{-1}$ )	$\Delta E_{(\text{obs}-\text{calc})}$ (cm $^{-1}$ )	$\delta_{\text{calc}}^a$
38		90 804.975(8)		0.675 67(4)
39		90 809.032(8)		0.675 66(4)
40	90 812.82(3)	90 812.784(8)	0.031	0.675 65(4)
41	90 816.24(3)	90 816.260(8)	-0.023	0.675 65(4)
42	90 819.53(3)	90 819.486(8)	0.040	0.675 64(4)
43	90 822.46(3)	90 822.487(8)	-0.029	0.675 64(5)
44	90 825.27(3)	90 825.282(8)	-0.013	0.675 63(5)
45	90 827.87(3)	90 827.890(8)	-0.016	0.675 63(5)
46	90 830.38(3)	90 830.328(8)	0.054	0.675 62(5)
47	90 832.56(3)	90 832.609(8)	-0.045	0.675 62(5)
48	90 834.81(3)	90 834.747(8)	0.065	0.675 61(6)
49	90 836.77(3)	90 836.754(8)	0.013	0.675 61(6)
50	90 838.69(3)	90 838.640(8)	0.045	0.675 61(6)
51	90 840.39(3)	90 840.415(8)	-0.025	0.675 60(6)
52	90 842.09(3)	90 842.087(8)	0.004	0.675 60(7)
53	90 843.57(10) <sup>b</sup>	90 843.664(8)	-0.099	0.675 60(7)
54	90 844.96(10) <sup>b</sup>	90 845.153(8)	-0.195	0.675 59(7)
55	90 846.39(10) <sup>b</sup>	90 846.560(8)	-0.170	0.675 59(8)
56	90 847.88(3)	90 847.893(8)	-0.009	0.675 59(8)
57	90 849.12(3)	90 849.154(8)	-0.034	0.675 59(8)
58	90 850.34(3)	90 850.351(8)	-0.016	0.675 58(8)
59	90 851.45(3)	90 851.486(8)	-0.036	0.675 58(9)
60	90 852.54(3)	90 852.564(8)	-0.024	0.675 58(9)
61	90 853.56(3)	90 853.589(8)	-0.027	0.675 58(9)
62	90 854.56(3)	90 854.565(8)	-0.005	0.675 58(10)
63	90 855.52(3)	90 855.494(8)	0.021	0.675 57(10)
64	90 856.38(3)	90 856.379(8)	0.003	0.675 57(10)
65	90 857.23(3)	90 857.223(8)	0.009	0.675 57(11)
66	90 858.06(3)	90 858.029(8)	0.027	0.675 57(11)
67	90 858.79(3)	90 858.798(8)	-0.008	0.675 57(11)
68	90 859.52(3)	90 859.534(8)	-0.015	0.675 57(12)
69	90 860.24(3)	90 860.237(8)	-0.002	0.675 56(12)

<sup>a</sup> Observed energies ( $E_{\text{obs}}$ ), calculated energies ( $E_{\text{calc}}$ ), and quantum defects ( $\delta$ ) for the [Be]2 $pn$  $p^3D_3$  ( $n = 3$  to 69) series, with their uncertainties (in parentheses, in units of the last decimal place of the value). All experimental energies, except for levels with  $n \leq 10$ , are from the present work;  $E_{\text{obs}}$  for  $n \leq 10$  are from [1]. In the fitting of the Ritz formula, the levels were weighted by inverse squares of their measurement uncertainties. See text for explanation of derivation of the  $E_{\text{calc}}$  uncertainties.

<sup>b</sup> These levels were excluded from the fitting of the Ritz formula (see text).

The fit residuals are satisfactory with the exception of those for  $n = 53, 54$ , and  $55$ . The energy region for these transitions suffered from both a scan rate non-linearity and a paucity of useful iodine calibration lines. After several unsuccessful attempts to calibrate these three lines, we concluded that they could not be calibrated to the accuracy of the other lines. They were therefore taken as outliers, assigned larger uncertainties, and removed from the data set for the fit for the series limit. Doing so led to a change in the resulting series limit barely within the final statistical error range of the ionization energy.

The fit was performed on a data set that consisted of the measured Rydberg state transition energies added to the intermediate state energy of  $60\,393.1693(14)\text{ cm}^{-1}$  [1]. The fit with a 4-term modified Ritz formula (see equation (1b) in [12]) yields  $90\,883.743(9)\text{ cm}^{-1}$  (with levels  $n = 53, 54$ , and  $55$  excluded) for the interval between the atomic ground state and the ionic  $^2P^{\circ}_{3/2}$  excited state, where the uncertainty includes the following contributions: the standard deviation of the fit with the given values of energies,  $0.005\text{ cm}^{-1}$ , the standard deviation ( $0.006\text{ cm}^{-1}$ ) of 500 fits (of the same Ritz formula) with the level energies randomly varied around their nominal values with normal distributions of a width corresponding to their measurement uncertainties, and a systematic uncertainty in the measured  $n \geq 6$  energies, estimated to be  $0.003\text{ cm}^{-1}$ . It should be noted that the original RITZPL code of Sansonetti [11] was modified by one of us [K] for estimating the uncertainty by random trials. Subtracting from the limit value the ionic ground-state fine-structure interval  $63.395\,09(2)\text{ cm}^{-1}$  [9] (with more significant figures than in our earlier work) gives the ionization energy of C I from the ground state to the ionic ground state as  $90\,820.348(9)\text{ cm}^{-1}$ . Table 1 below shows the results for observed and fitted values of the Rydberg energies above the ground state of the neutral atom, as well as the calculated quantum defects. Calculated values of unobserved energy levels are included, since they are accurate enough to be of use in future studies involving photoabsorption spectrum of atomic carbon. Uncertainties of the calculated energies  $E_{\text{calc}}$  for  $n < 6$  are equal to the standard deviations of 500 random trial fits for each level. For higher  $n$ , the above random-trial uncertainty estimate was combined in quadrature with the standard deviation of the fit for the limit value,  $0.005\text{ cm}^{-1}$ , and an estimated systematic uncertainty of the observed  $n \geq 6$  levels,  $0.003\text{ cm}^{-1}$ .

## 5. Conclusions

We have re-analyzed our previously published Rydberg energy measurements for C I through re-assessment of our observed  $2pnp\ ^3D_3$  series Rydberg transition energies, utilizing critically analyzed and improved energy values for the molecular-iodine calibration lines to determine the Rydberg transition energies, and recently improved available data for associated energy intervals in the carbon atom. Our principal result is a new value for the ionization energy of the neutral carbon atom,  $90\,820.348(9)\text{ cm}^{-1}$  or  $11.260\,2880(11)\text{ eV}$  in accordance with the 2014 CODATA recommended conversion factor  $1.239\,841\,9739(76) \times 10^{-4}$  for  $\text{cm}^{-1}$  to eV [13], with a precision about 9 times better than our previously published result. Our analysis shows that, in order to produce the most accurate  $\text{I}_2$ -based calibrations possible with probe lasers of finite linewidth, a great deal of care must be taken to treat complications in the iodine calibration spectrum such as blended lines and unresolved hyperfine structure.

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