we have the following three solutions of (56):

$$E_1=-2C/3Z_1^*Z_2^*R^3, \quad (^1\Sigma_u),$$
$$E_2=C/3Z_1^*Z_2^*R^3, \quad (^1\Pi_u), \qquad (58)$$
$$E_3=-C/3Z_1^*Z_2^*R^3, \quad (^3\Pi_u).$$

A comparison with the corresponding results in the uncoupled representation (II.8)–(II.10) and an analysis of the state functions show that these energy curves correspond to a $^1\Sigma_u$, a $^1\Pi_u$, and a $^3\Pi_u$ state, respectively. In Fig. 1 we have plotted one of the exact solutions of (56) for the interaction of two H atoms (heavy line), together with the corresponding energy curves in the uncoupled and coupled representation. It is seen that the exact energy curve merges into the $\Pi_u(1S,2P_1)$ $\{^1\Pi_u,^3\Pi_g\}$ curve of (II.9) at small internuclear separations, and it approaches asymptotically the energy curve of the $1_u(1S_{\frac{1}{2}-\frac{1}{2}},2P_{\frac{3}{2}\frac{3}{2}})$ state at large R. The solution $E_2(^1\Pi_u)$ corresponds to this curve at small internuclear separations.

It should be noted that the symmetry of the state functions under inversion through the center of the molecular system does not change when the spin-orbit interactions are included. In our specific case, all the energy curves obtained from the generalized perturbation treatment correspond to u states.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor Henry Margenau for suggesting this problem and also for the many helpful discussions during the course of this work. Financial support for this research from the Office of Naval Research is gratefully acknowledged.

PHYSICAL REVIEW VOLUME 125, NUMBER 5 MARCH 1, 1962

Structure and Photodetachment Spectrum of the Atomic Carbon Negative Ion*

MICHAEL L. SEMAN AND LEWIS M. BRANSCOMB
National Bureau of Standards, Washington, D. C.
(Received October 17, 1961)

The continuous absorption (photodetachment) spectrum of a beam of atomic carbon negative ions from a hot cathode arc was measured in the spectral region 0.4 to 2.6 μ. Between 0.4 and 0.8 μ the C^- photodetachment cross section was measured relative to that for O^- and was found to be almost independent of wavelength, consistent with the assignment of ^4S to the C^- ground state. In this region the C^- cross section is approximately twice that for O^-. The variation of the absorption near one micron is consistent with the expected threshold behavior and yields a value for the ground-state binding energy (carbon electron affinity) of 1.25±0.03 ev. Weak absorption in the region from 1 to 2.6 μ is felt to demonstrate the stability of a metastable negative-ion state, probably C^- $1s^22s^22p^3\,^2D$. No such absorption is observed at wavelengths longer than the ground-state threshold in O^-, in which metastable states are not expected.

I. INTRODUCTION

THIS measurement of the continuous absorption coefficient (or photodetachment cross section) for the atomic carbon negative ion, C^-, completes a series of studies of the atomic negative ions of interest as sources of opacity in stellar atmospheres. Data for H^- and O^- have been reported elsewhere.[1,2] A general discussion of the possible contribution of negative ions other than H^- to stellar opacities suggests that ions such as O^- and C^- are likely to be important in cooler stars of unusual composition.[3]

Other than the present results, no measurements and no significant calculations of the photodetachment cross section for C^- have been published. The experimental evidence regarding the binding energy of the ground state consists of an estimate from the rate of sublimation of C^- ions from a carbon filament[4] and two measurements (unpublished) of the difference between the electron affinities of C and O obtained by electron impact in CO.[5,6] These values, which are summarized in Table III, indicate a threshold for photodetachment from the C^- ground state in the region of 1 μ, corresponding to a binding energy in the vicinity of 1.2 ev.

With regard to the existence of states of C^- other than the ground state there is even less information. Theoretical and semiempirical evidence[7,8] suggests that

* Supported in part by the Office of Naval Research.
[1] S. J. Smith and D. S. Burch, Phys. Rev. **116**, 1125 (1959).
[2] S. J. Smith, *Proceedings Fourth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1960), p. IC219.
[3] L. M. Branscomb and B. E. F. Pagel, Monthly Notices Roy. Astron. Soc. **118**, 258 (1958).
[4] R. E. Honig, J. Chem. Phys. **22**, 126 (1954).
[5] C. R. Lagergren, Ph.D. thesis, University of Minnesota, 1955 (unpublished).
[6] M. A. Fineman and A. Petrocelli (private communication) and Bull. Am. Phys. Soc. **3**, 258 (1958).
[7] H. S. W. Massey, *Negative Ions* (Cambridge University Press, New York, 1950), 2nd ed.
[8] D. R. Bates, Proc. Roy. Irish Acad. **A51** (1947) and D. R. Bates and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A68**, 540 (1955).

atomic negative ions have very few if any excited states below the continuum. Experimentally this has been supported only by negative information, for there has been no experimental evidence for atomic negative ions with more than one singly excited state. (Several such reports were later reinterpreted or unconfirmed.)[9] As Bates and Moiseiwitsch[8] pointed out, it is unlikely that excited electronic configurations of light ions will be bound, but excited terms of the ground-state configurations may be bound in certain cases. The most favorable case was found to be Si^-. In such cases, the excited term will be metastable because of differences in multiplicity from the ground state. Thus we may not expect permitted line spectra in these ions, but may expect the excited states, if bound, to be populated when the ions are generated in a high-temperature source. One may look for evidence for such states by looking for continuous absorption at wavelengths longer than the ground-state detachment threshold. The presence of such absorption is conclusive evidence for a state of smaller binding energy than the ground state; its absence is suggestive but inconclusive evidence that excited states are not populated and suggestive that they do not exist.

II. THE EXPERIMENT

In principle the apparatus used was similar to the one described by Smith and Branscomb.[10] A beam of mass-analyzed negative ions passes through an intense flux of photons. The ratio of the photo-ejected electron current to the product of the ion current and the photon flux is measured and is related to the photodetachment cross section. In applying this method to C^- for which suitable ion sources with yields in the range of 10^{-7} ampere do not exist, a choice had to be made between an attempt to develop such a source and the modification of the apparatus so that the minimum usable ion current could be reduced from 10^{-8} ampere[10] to 10^{-10} ampere. The latter plan was adopted and achieved with the reaction chamber shown in Fig. 1.

The ion beam passes through the focus of the light beam (from left to right in the figure) which was modulated at 450 cps. As in previous experiments,[10] the light flux was monitored externally. A 15-v/cm electric field and a 40-gauss vertical magnetic field separated the photodetached electrons from the ion beam. They were then accelerated to an energy of 500 ev and focused on the cathode of a 10-stage Ag-Mg electron multiplier. The reaction chamber and its components were constructed entirely of refractory metals, and metal gaskets provided the vacuum seals. A 300°C bakeout for 12 hr insured that a pressure of 1×10^{-7} mm Hg existed in the reaction region during experiments. This reduction

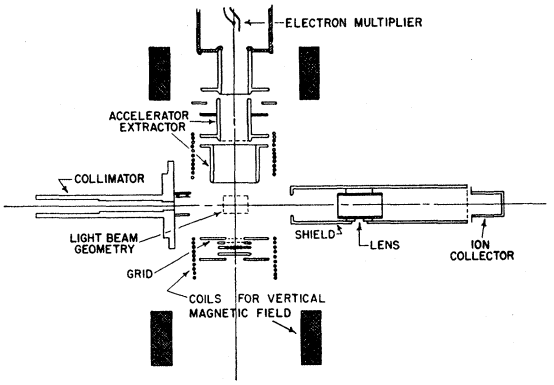

FIG. 1. Schematic diagram of the reaction chamber used in the present experiment.

in background pressure by a factor of about 10 over the previous apparatus[10] increased the signal-to-noise ratio in the experiment by reducing the noise contribution of the electrons collisionally detached by the background gas molecules. The replacement of an electron collector and preamplifier by the electron multiplier permitted the use of smaller ion beams which produced correspondingly smaller photodetached electron currents. The smallest signals reported in this paper corresponded to electron currents of about 10^{-18} amp.

The ion source used in this work was a hot cathode arc discharge illustrated in Fig. 2. At the suggestion of Fineman, the arc was run in about 50-μ pressure of CO. It provided a current of up to 3×10^{-9} amp (more typically 5×10^{-10} amp) of C^- after mass analysis, deceleration, and collection at the ion collector. The current remained constant for periods of up to half an hour without readjustment of the source. A 20-mil hairpin-shaped wolfram wire filament provided 400 ma of arc current with a 50-v drop between anode and cathode. The arc column was confined by a series of insulated stainless steel disks containing holes which

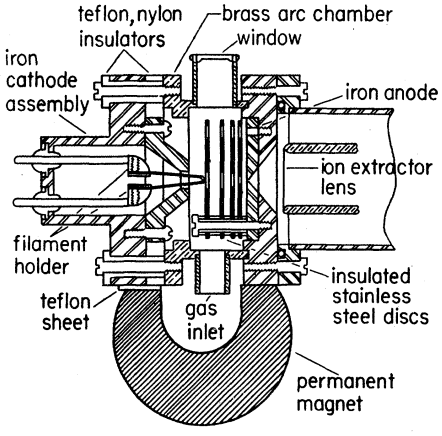

FIG. 2. Schematic diagram of the hot cathode arc discharge negative-ion source.

[9] L. M. Branscomb, *Advances in Electronics and Electron Physics* edited by L. Marton (Academic Press, Inc., New York, 1957), Vol. 9.

[10] S. J. Smith and L. M. Branscomb, Rev. Sci. Instr. **31**, 733 (1960).

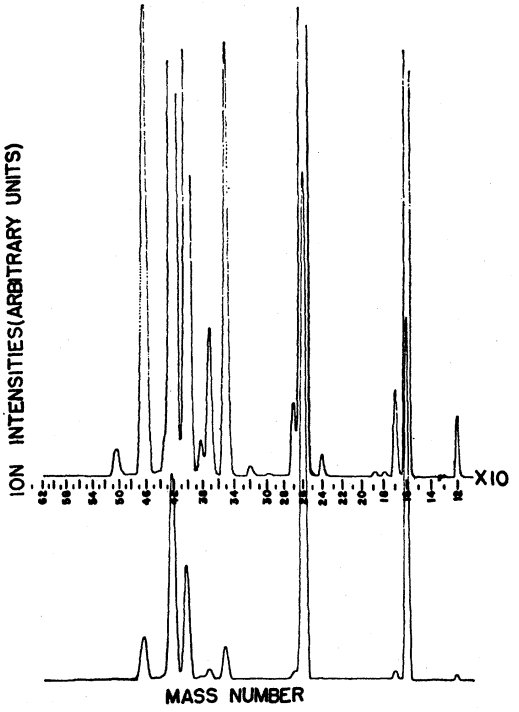

FIG. 3. Mass spectrum of negative ions produced using Co as the primary gas in the arc discharge source.

decreased in diameter from 5 mm to 1 mm from filament to anode. An axial magnetic field (about 200 gauss) made it possible to strike the arc. Higher magnetic fields were not as helpful as they are for positive-ion sources, presumably because the confinement of the electrons on axis tends to displace the negative ions from the axis and to destroy the negative ions in the arc channel as the electrons are acclerated by the fields of the extraction lens. Through the window, when the source is operating properly, an intense blue plasma may be seen located in the center of the insulated disk nearest the anode.

The only precaution taken with regard to gas purity was to keep chemically pure CO gas continually flowing through the arc during operation. It is apparent from Fig. 3 that the negative-ion spectrum strongly accentuates the effect of highly electronegative contaminants. The spectrum in Fig. 3 is a display of collected negative ion current versus magnetic field in the mass spectrometer operated at fixed accelerating voltage. Table I gives the proposed identifications of the peaks. It can be said that mass 12 (C^-) was only a trace ion in the spectrum. There was, nonetheless, sufficient current for the experiment with no danger of contamination from other ion species.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. C^- Photodetachment Cross Section between 0.4 and 0.8 μ

In this spectral range a preliminary investigation showed that the cross section for photodetachment varied slowly with wavelength, and it was legitimate to use the band-pass filters in the light beam which were used in the earlier study of O^-. For each band of wavelengths the relative detachment probabilities for C^- and O^- were measured. The O^- current was attenuated so that the signals from the two ions were comparable. Correction of these ratios for the relative velocities of the two ions (which were compared at the same energy) yields the relative photodetachment cross sections for the ions. The C^- data are shown by the circles in Fig. 4, using the O^- data of Smith[2] for normalization.

TABLE I. Mass spectrum identity assignments.

Mass	Assignment	Mass	Assignment
1	H^-	30	NO^-
12	C^-	32	O_2^-
16	O^-	35	Cl^-
17	OH^-	37	Cl^-
18	$(O^{18})^-$	40	CN_2^-
19	F^-	42	CNO^-
26	CN^-	46	NO_2^-
27	$C^{13}N^-$		

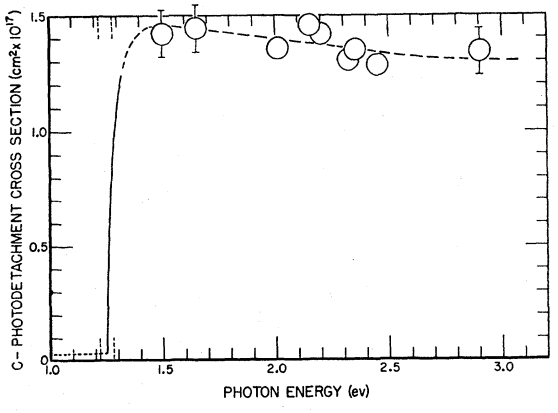

FIG. 4. (i) Circles (whose diameters indicate errors) and circles with error bars represent C^- cross-section measurements relative to O^-. (ii) Solid line represents our best fit to the C^- ground-state threshold data. (iii) Lower dashed line represents absorption ascribed to a metastable state of unknown population.

Since C^- is isoelectronic with N, it is presumed to have a ^4S ground state. Under this assumption the only possible transition is $^4S \rightarrow {}^3P$. If the ground state were not ^4S but ^2D one would expect that two transitions which should have cross sections of nearly equal magnitude ($^2D \rightarrow {}^3P$ and $^2D \rightarrow {}^1D$) would be possible,[11] the threshold for the two being 1.26 ev apart. Since we observed no second threshold at 1.26 ev above the first, we conclude that the ground state is ^4S. The threshold

[11] D. R. Bates and H. S. W. Massey, Trans. Roy. Soc. (London) A239, 269 (1943).

for the process,

$$h\nu + C^-(^4S) \rightarrow C(^3P) + e, \quad (1)$$

provides a measure of the electron affinity of carbon, which we will show later is about 1.25 ev.

B. C^- Spectrum between 0.8 and 2.6 μ

As band-pass filters of progressively longer mean wavelength were inserted in the photon beam the detachment signal was found to decrease very rapidly in the region 0.8 to 1.0 μ. It was quite obvious that the primary absorption threshold lay in this region, and that the spectrum was varying too rapidly to permit data analysis assuming the filters are effectively monochromatic. The same procedure was adopted which had been used in the analysis of the O^- threshold region.[12] Transmission filters with varying cutoffs which progressively cut off short wavelengths more and more toward the infrared were used. The idea was to continue until all of the radiation was of sufficiently long wavelength that no further signal could be detected. The threshold region would then be bracketed. With accurate calibration of the filters and a theoretically correct expansion of the cross section in terms of the undetermined threshold wavelength one could then determine numerically the best value of the threshold wavelength and the parameters which describe the shape of the cross section near threshold.

TABLE II. Corrected and uncorrected measured detachment probabilities for the various optical filters used.

Filter	P_i (arbitrary units)	P_i (corrected)
K+143	0.492±0.004	0.479±0.004
K+144	0.320±0.006	0.305±0.006
N+0	0.209±0.007	0.166±0.007
N+145	0.066±0.006	0.036±0.006
N+148	0.026±0.005	0.003±0.005
N+150	0.012±0.003	
N+148+157	0.008±0.002	
C+0	0.350±0.014	0.190±0.014
C+150	0.160±0.006	
C+150+157	0.100±0.003	
C+150+151	0.079±0.005	
C+150+164	0.063±0.004	
C+150+159	0.049±0.005	

Table II gives the results in arbitrary units for the filters whose transmittances are shown in Figs. 5 and 6. With the filter series identified by the letters N and K, it is seen that the point of negligible signal is very nearly obtained with filter "N+148." These filters (Fig. 5) embrace the region of the ground-state threshold. However, the signals persisted to longer wavelengths, and the "C" series of carbon tetrachloride-cooled filters clearly showed that some absorption continued at least as far as 2 μ. This weak absorption beyond the primary threshold constitutes the evidence for an excited, metastable negative-ion state.

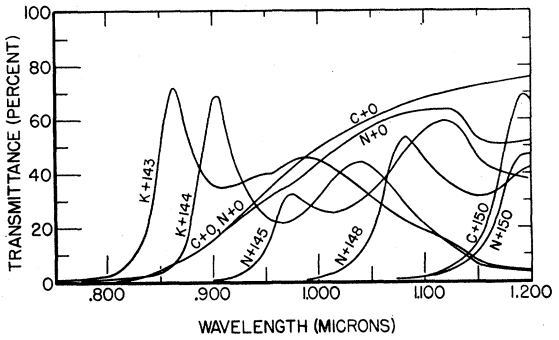

FIG. 5. Transmissions of optical filters used for studying the C^- ground-state threshold.

Before attempting to determine the ground-state threshold and to investigate the possible effect of the infrared absorption on this determination it was necessary to show that the infrared effect was not spurious. It was found to be quite reproducible for each filter combination, and the signals had the proper proportionality to ion current and photon flux. In order to prove that a residual filter transmission of a fraction of a percent in the 0.8-μ region (where the cross section is large) was not responsible for the signals seen with filters allegedly transmitting only in the infrared, the transmittances of these filters were carefully measured. Figure 7 shows that the filters do not indeed have a transmittance above 0.01% in this region. The light "leak" effect is quite negligible. A final check proved that the effect is a property of the C^- ions, and not of the apparatus. The absorption on the red side of the threshold in O^- was reinvestigated using the same technique. This will be described in a later section, but the result clearly shows no measurable effect in O^-.

Neglecting the infrared effect for the moment, it was found from the threshold filters of Fig. 5 which gave the largest signals, that the ground-state threshold lay near 1.2 ev. (A preliminary result of 1.18±0.05 ev was re-

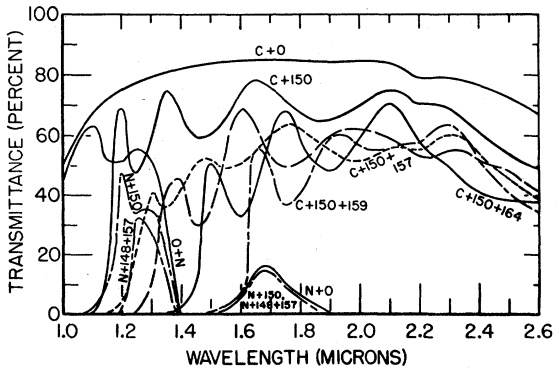

FIG. 6. Transmissions of optical filters used for studying the C^- excited state.

[12] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. 111, 504 (1958).

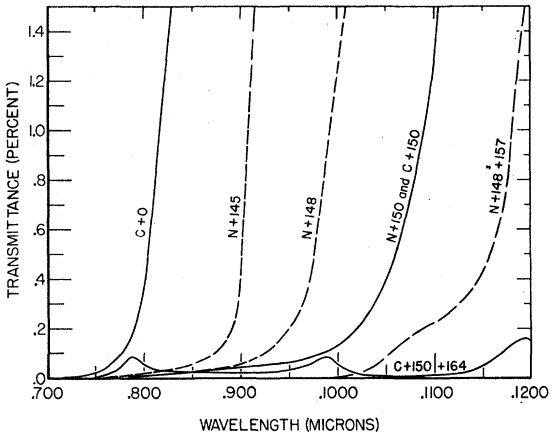

FIG. 7. Transmissions of filters in the spectral region where a contribution from the absorption of the $C^-(^4S)$ state might have been responsible for the signals ascribed to $C^-(^2D)$ absorption.

ported.)[13] In view of this and the results of the investigation of possible "leaks," it was concluded that the signals obtained from the filters whose transmissions are shown in Fig. 6 (except $C+0$ and $N+0$), were due to absorption on the long-wavelength side of the ground-state threshold. Unfortunately there was not sufficient signal-to-noise ratio to investigate the infrared effect with band-pass filters which did not overlap in wavelength. (The data reported here result from electronic integrations of signals for up to 1 min.) As a consequence we tested the consistency of the data with the assumption of an absorption coefficient which varies linearly with wavelength above a threshold wavelength λ_1:

$$\begin{aligned} \sigma &= a+b\lambda, \quad \lambda<\lambda_1 \\ \sigma &= 0, \qquad \lambda>\lambda_1. \end{aligned} \tag{2}$$

The detachment probabilities given in Table II are related to the absorption coefficient σ by

$$P_i=\int_0^{\infty}\Phi\lambda T_i\sigma d\lambda=\int_0^{\lambda_1}\Phi\lambda T_i(a+b\lambda)d\lambda. \tag{3}$$

Here Φ is the energy flux in the unfiltered radiation of the carbon arc light source, λ is the wavelength, and T_i is the transmittance of the ith filter. Since the quantities Φ and T_i can be measured in the laboratory, the least-squares fit to the straight line function shown in Fig. 8 provides a determination of the coefficients a and b for each of the three values of λ_1 which were tried. Since Φ is small for $\lambda>2.6\,\mu$, the contribution to P_i for wavelengths greater than $2.6\,\mu$ in Eq. (3) are negligible. The errors in the data are such that one can only conclude from Fig. 8 that any of the three possibilities shown are acceptable, but one cannot reduce the slope of the straight line to zero or a negative value without doing serious violence to the statistical errors in the observations. On theoretical grounds one might prefer the line of lowest slope, for it corresponds to a binding energy of the metastable state of less than 0.5 ev. If one extrapolates the straight line to shorter wavelengths, one can again use (3) with the transmittances T_i of the filters as shown in Fig. 5 to derive detechment probabilities P_i due to the metastable state, which must be substracted from the observed total P_i's for the ground-state threshold filters. The third column of Table II shows the corrected values of P_i, assuming that the infrared effect is described by the curve of lowest slope in Fig. 8. The correction is seen to be quite small. If one takes either of the other assumptions in Fig. 8 ($\lambda_1=2.1$ or $1.8\,\mu$), the extrapolated straight line intersects the abscissa at longer wavelengths than $1\,\mu$, making the corrections in general much smaller for those threshold-region filters which cut off around 1.1 to $1.2\,\mu$. Thus we draw no conclusions about the binding energy of the metastable state, or about the shape of the absorption coefficient of ions in that state, but we feel justified in concluding that the proper correction to the observed data in the threshold region for use in determining the binding energy of the ground state lies somewhere between zero and the corrections implied by extrapolation of the curve of lowest slope in Fig. 8.

C. Threshold for Photodetachment from the C^- ^4S Ground State

To determine the wavelength of the threshold for photodetachment from the C^- ground state λ_0 we must again solve a set of simultaneous equations like (3). This time we have six equations corresponding to the filters for which corrected values of detachment probability, p_i^{cor}, are given in Table II. For the analytical form of the expansion of the cross section near threshold we use the same form which was successful in the case

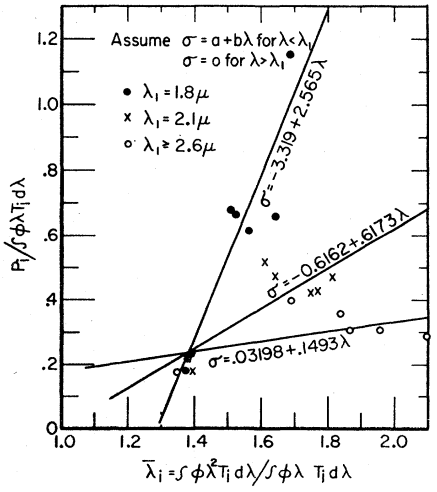

FIG. 8. Least-squares fit to determine the coefficients a and b in Eq. (3), where P_i is the photodetachment probability and $\sigma=a+b\lambda$ is the assumed form for the infrared cross section.

[13] L. M. Branscomb, and M. Seman, Bull. Am. Phys. Soc. 6, 356 (1961).

of O^-, and which is justified[12] on the same theoretical basis:

$$\sigma=\alpha\lambda^{-1}(\lambda^{-1}-\lambda_0^{-1})^{\frac{1}{2}}+\beta\lambda^{-1}(\lambda^{-1}-\lambda_0^{-1})^{\frac{3}{2}}. \quad (4)$$

For each value of λ_0 for which calculations were made we determined the values of α and β which gave the best fit, and found the standard deviation of this fit. The different values of P_i were given equal weight in this calculation since the variation of the standard deviations given in Table II does not justify assigning different weights. A standard deviation of 0.006 was used for all of the data.

If we ignore for the moment the variation of the standard deviation of the fit with different values of λ_0, we may examine the shape of the cross-section curves corresponding to these "best" values of α and β. From Fig. 9 one sees that $\lambda_0=1.00\,\mu$ provides a slope which gives much better continuity with the 0.4 to 0.8 μ data than does either $\lambda_0=0.98\,\mu$ or $\lambda_0=1.01\,\mu$. However, we have not relied upon this observation in selecting the best value of λ_0, but have examined the wavelength dependence of the standard deviation of the fit, S. Figure 10 shows two curves. Curve A was derived from the six values of P_i^{cor}. Curve B was determined with no correction to the data for the infrared effect. In this case the data from filters $C+0$ and $N+148$ were omitted as the infrared effect is obviously appreciable. The central value is 0.99 μ, which corresponds to 1.25 ev.

In order to determine the statistical uncertainty which should be associated with the wavelength of the minimum of S we "repeated" the experiment mathematically by randomly varying the P's around the quoted experimental values. For this process a standard deviation of the experimental P_i's of 0.006 was used. Although exact limits for the uncertainty in λ_0 cannot be given, these random sampling experiments indicate that the three-standard-deviation limit for λ_0 is approximately 0.01 μ. Note that this is of the same order as the uncertainty imposed by the impossibility of fully correcting the data for the contribution of absorption from the excited state. Accordingly, we assign to the threshold wavelength the value $0.99\pm0.02\,\mu$ and to the carbon electron affinity the value 1.25 ± 0.03 ev.

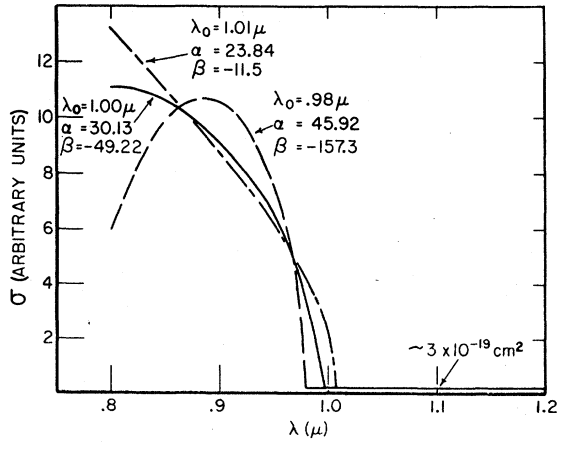

FIG. 9. Various C^- threshold cross sections of the form given in Eq. (4) for different least-squares determinations of α and β, and for various values of λ_0.

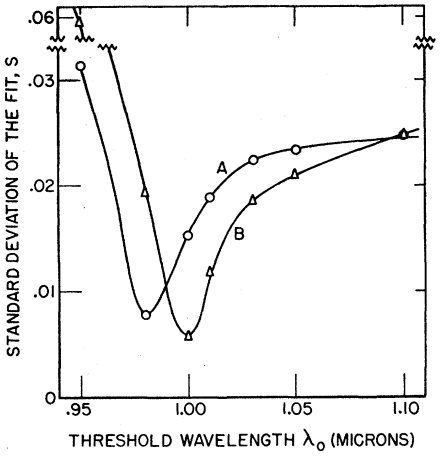

FIG. 10. Standard deviations of the P_i's from $\int\Phi T_i\sigma\lambda d\lambda$, where σ is given by Eq. (4). Curve A was determined by substracting the contribution from the infrared absorption assuming $\sigma=0.03198+0.1493\,\lambda$ (open circles). Curve B was determined with no change of the original experimentally determined P_i's (triangles).

In Fig. 4 the solid curve shows the threshold form of the C^- cross section. The dashed portion at longer wavelengths is the extrapolated contribution from the metastable state. This cannot be considered part of the "cross section," for its magnitude is the product of the photodetachment cross section from the metastable state and population of the metastable ions. We have no way of estimating either of these quantities independently. However, it seems unlikely that the absorption cross section of the metastable state is much different from that of the ground state. We presume that the small contribution of the infrared effect (about 3×10^{-19} cm^2 in our beam) is caused by the fact that the ions in our beam are predominately in the ground state.

D. An Upper Limit to the Photodetachment Absorption Coefficient on the Long-Wavelength Side of the O^- Threshold

The discovery of evidence for an excited metastable state in C^- led us to investigate O^- again in order to place an upper limit on the absorption to long wavelengths from the ground-state threshold. Filters $N+0$ and $C+0$ (see Fig. 5) were used, and the results were interpreted using the O^- ground-state cross section given by Smith.[2] Assuming a constant cross section from the O^- threshold near 0.9 μ out to the apparatus cutoff at 2.6 μ, we find

$$\sigma_0\simeq-1.71\pm2.68\times10^{-21}\text{ cm}^2. \quad (5)$$

TABLE III. Various determinations of the atomic-carbon electron affinity.

Author	Method	Value (ev)
Present result	Photodetachment of electrons from C^-	1.25±0.03
Lagergren[a]	Electron impact on CO	1.11±0.05
Fineman and Petrocelli[b]	Electron impact on CO	1.33±0.18
Honig[c]	Mass spectrometer analysis of C^- sublimed from a carbon filament	1.2
Edlén[d]	Isoelectronic extrapolation	1.24
Johnson and Rohrlich[e]	Isoelectronic extrapolation	1.21

[a] See reference 5. [b] See reference 6. [c] See reference 4.
[d] See reference 14. [e] See reference 15.

This is two orders of magnitude smaller than the effect in C^- and gives us confidence that the C^- result is not spurious. Since O^- has only one term in its ground-state configuration, and since Bates and Massey[11] found it unlikely on theoretical grounds that excited configurations are bound, we did not expect to find absorption beyond the ground-state threshold in O^-.

IV. BINDING ENERGIES DETERMINED BY ISOELECTRONIC EXTRAPOLATION

The most successful estimates of electron affinities by extrapolating the properties of neutral atoms and positive ions are obtained by Edlén[14] and by Johnson and Rohrlich.[15] Their predictions and the experimental results referred to in the Introduction are shown in Table III. The agreement between our observations and the isoelectronic extrapolations is quite remarkable and probably to some extent fortuitous. It encourages us to apply the same equations for the "center of gravity" or the ^2D states of the ground configuration of the isoelectronic atoms and ions. The result[16] is a prediction of -0.05 ev binding. The accuracy of the extrapolation is probably such that one can only conclude that it is likely that the ^2D state lies very near the continuum. Unfortunately the available data on the ^2D excitation potentials of highly ionized members of the isoelectronic sequence are not sufficiently accurate to permit the use of an equivalent expression to that given by Edlén, using term differences and not depending on the ionization potentials.

As pointed out by Bates and Moiseiwitsch,[8] the light ion containing the most strongly bound metastable excited state is probably Si^-. Similar calculations to those for C^- give for Si^- the following binding energies: 1.46 ev for ^4S; 0.57 ev for ^2D; and 0.005 ev for ^2P. There is some reason to hope that the threshold for photodetachment from Si^- ^2D may lie within the spectral range of our instrumentation.

ACKNOWLEDGMENTS

We are particularly indebted to M. A. Fineman, who while a NRC-NAS Research Associate at the National Bureau of Standards did the original research on the C^- ion source and who participated in early phases of the experiment. E. C. Beaty guided us in the use of electronic integrators, which provided a substantial improvement in signal-to-noise ratio. J. Cameron and M. Dannemiller carried out the statistical analysis of the data. M. N. Inscoe and J. Schleter provided precision measurements of the filter transmittances. S. J. Smith was intimately involved in the design and construction of the new reaction chamber.

[14] B. Edlén, J. Chem. Phys. **33**, 98 (1960).
[15] H. R. Johnson and F. Rohrlich, J. Chem. Phys. **30**, 1612 (1959).
[16] For this estimate we used the ionization potentials given by Edlén[14] and excitation potentials recommended to us by C. M. Moore-Sitterly.