Letters to the Editor

Electron Affinity of Atomic Oxygen

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(Received March 3, 1955)

THE electron affinity of atomic oxygen has been deduced experimentally by other investigators from the study of electron attachment at a hot filament[1,2] and from dissociative attachment in a mass spectrometer.[3-6] These methods have yielded consistent results: 2.33 ± 0.03 ev,[2] 2.2 ± 0.2 ev,[3] 2.0 ± 0.5 ev,[4] 2.09 ± 0.4 ev,[5] and 2.2 ± 0.2 ev.[6] Theoretical calculations using a self-consistent field can give only a lower limit of 0.5 ev.[7] Recent empirical isoelectronic extrapolations by Moiseiwitsch[8] and Bates and Moiseiwitsch[9] predict 1.12 ev and 2.0 ev, respectively.

We have made a direct determination of the O^- affinity by observing the threshold and measuring the cross section for photodetachment of an electron from the O^- ion. First applied to H^-,[10,11] this method uses a beam of mass-separated negative ions illuminated by a beam of radiation of measured intensity and spectral distribution, $\phi(\lambda)$. A current of free electrons, detached from the ions in the region of intersection of the photon and ion beams, is collected and measured.

The wavelength dependence of the cross section $\sigma(\lambda)$ is tested with water-cooled glass filters, whose transmissions $T_n(\lambda)$ are shown in Fig. 1. The probabilities per ion photodetachment, averaged from 23 experiments,
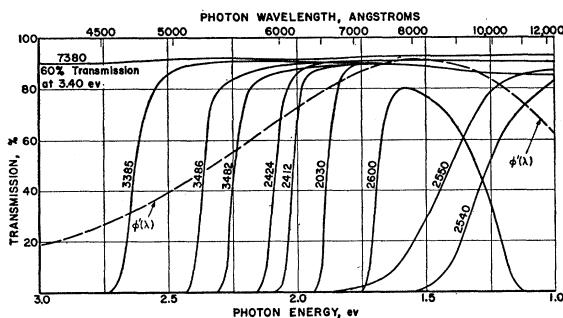
TABLE I. Experimental photodetachment probability, P_{exp}, for O^- with 9 glass filters; and P_{calc} using Eq. (1) and the $\sigma(\lambda)$ given in Fig. 2 for a 1.45-ev affinity.

Corning filter No.	$P_{exp}\times10^5$ [a]	$P_{calc}\times10^5$	$(P_{exp}-P_{calc})\times10^5$
7380	1.66 ± 0.02	1.686	-0.02
3385	1.50 ± 0.04	1.502	0.00
3486	1.35 ± 0.03	1.350	0.00
3482	1.25 ± 0.04	1.243	0.01
2424	1.08 ± 0.05	1.100	-0.02
2412	0.948 ± 0.07	0.985	-0.04
2030	0.820 ± 0.03	0.790	0.03
2600	0.377 ± 0.04	0.375	0.002
2550	0.074 ± 0.016	0.0811	-0.007
2540	<0.02	0.0	<0.02

[a] Each datum is the mean value from 23 experiments, and the average deviation of these measurements from the mean.

are given in Table I. For the nth filter, the experimental probability is related to $\sigma(\lambda)$ by

$$P_n = 1.703\times10^{13}\int \sigma(\lambda)\phi'(\lambda)T_n(\lambda)\lambda d\lambda. \qquad (1)$$

Here $\phi'(\lambda)$ is normalized $[\int \phi'(\lambda)d\lambda=1]$, and λ is in microns. The filters with cutoffs above 1.9 ev were used in pairs to give the circled points of Fig. 2, each point corresponding to the difference of two P's, $\sigma(\lambda)$ being assumed slowly varying. The average deviation of these points is quite large because of the noise level and the temperature dependence of the filter transmissions, but the points are not independent, as shown by (1).

The large detachment signal with filter 2600 shows that the threshold lies substantially below 1.75 ev. With filter 2540 no signal is observed $[\sigma(\lambda)<1\times10^{-19}\text{ cm}^2]$, giving a threshold above 1.35 ev. A monotonic function, nearly parabolic, has been fitted to the data of Table I. The upper limit to the affinity for a monotonic function is about 1.52 ev. If the threshold is to lie above 1.52 ev, a narrow resonance peak followed by a minimum seems to be required so that (1) and Table I can be satisfied.
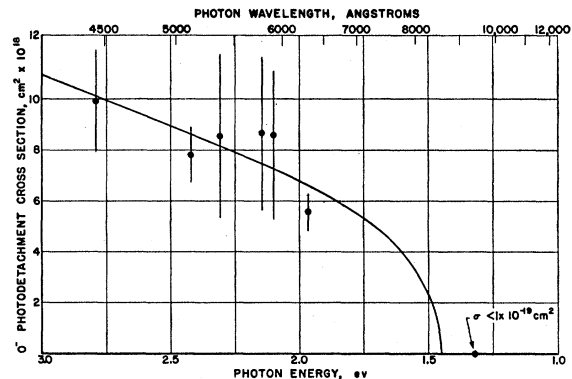

FIG. 1. Transmissions of filters used to determine wavelength dependence of O^- photodetachment cross section. The dashed curve is the normalized spectral distribution of the radiation source with the ordinate taken as 1 (micron)$^{-1}$ = 100 percent.

FIG. 2. Cross section for photodetachment of electrons from O^-. The solid curve is not extrapolated, but is the best fit to the data of Table I for a monotonic function and is thus not uniquely determined.

There is no evidence of a maximum near the threshold, although this possibility is not excluded.

The resolution of the mass separator was sufficient to exclude O_2^-, which has a detachment threshold below 1 volt and a cross section of about 0.4×10^{-18} cm² at 8000 A. Mass peaks of impurities at 17 and 19 amu were about 0.2 percent of the $(O^{16})^-$ peak, and thus comparable with the $(O^{18})^-$ peak, as determined with a high-resolution analyzer after the detachment chamber.

The O^- affinity given by our data is 1.45 ± 0.15 ev, the estimated uncertainty being related to the shape of $\sigma(\lambda)$ very near the threshold. This result is in unresolved conflict with previous experiments,[1-6] although not inconsistent with theoretical extrapolations.

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Orthogonality of the Furry-Sommerfeld-Maue Wave Functions and their Use in Perturbation Theory

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(Received January 13, 1955; revised manuscript received March 15, 1955)

IN a recent paper on internal pair formation, Horton and Phibbs[1] assert that the Furry-Sommerfeld-Maue wave functions[2-4] for a Dirac particle in a Coulomb field are not orthogonal, and that for any process calculated by perturbation theory using these wave functions, the interaction matrix element must be modified accordingly.

It is our contention that the Furry-Sommerfeld-Maue wave functions are orthogonal in the usual sense, at least to the order of magnitude to which they are valid, and that perturbation theory does not need to be modified in any way on account of their use.

Horton and Phibbs prove in their Appendix I that the wave function of a positive electron with energy E_+ which satisfies the iterated Dirac equation with a Coulomb potential is not orthogonal to the wave function of a negative electron with energy E_- which satisfies a similar iterated equation. This is to be expected, since the positive and negative electrons have different Hamiltonians, the Coulomb terms being of opposite signs. As will be seen below, the lack of orthogonality of wave functions appropriate to different Hamiltonians is irrelevant to the problem.

In their Sec. III Horton and Phibbs go through the standard derivation of time-dependent perturbation theory, but because of the assumed applicability of their Appendix I, end up with a modified interaction matrix element [their Eqs. (16) and (18)]. The results of their Appendix I are not applicable, however, because, as is customary, they use as their unperturbed wave functions the various eigenfunctions of a *single* Hamiltonian. In the pair production problem, this demands interpreting the initial state as that of a negative electron with negative energy and the final state as that of a negative electron of positive energy.[5] Horton and Phibbs make the error of identifying the initial state wave function with that of a positive electron of positive energy satisfying the iterated Dirac equation, and so are led to use the irrelevant Appendix I to alter perturbation theory.

It is a straightforward matter to show that for a given sign of the electronic charge, wave functions satisfying both the ordinary and iterated Dirac equations of two different energies are orthogonal in the usual sense. Since the Furry-Sommerfeld-Maue wave functions are approximate solutions of these equations, they will be orthogonal to the same order of approximation. Consequently no modification of perturbation theory is necessary when these wave functions are used.

It should be mentioned that the main conclusions of Horton and Phibbs on the validity of the Born approximation in internal pair production are unaffected.

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[5] See Sec. V of reference 4 for this argument applied directly to the Furry-Sommerfeld-Maue wave functions.

Comments on Straumanis' Concepts Regarding Avogadro's Number*

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(Received December 10, 1954; revised manuscript received February 21, 1955)

STRAUMANIS[1] has advocated that Avogadro's number be defined in terms of a standard crystal, "purest calcite," until such time as a "truly reliable" value may be established. This suggestion introduces a new variable into the field of the atomic constants: the ratio of the true value to the standard value. Although his proposal is based on a consideration of operational definitions for physical quantities, it is not in accord with the philosophy of simplification of concepts. It is, however, strongly influenced by the existence of discrepancies in the values obtained for Avogadro's number (both by direct measurement and