SMALL FREE NEGATIVE IONS

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I. Introduction

This article surveys the restricted subject of properties of isolated atomic and small molecular negative ions. By so defining our subject, we include in our discussion electron affinities, electronic states, and optical properties, and the experimental and theoretical methods for studying these properties. We exclude from our discussion the vast group of problems associated with large polyatomic negative ions and with most of the rich subject of collision processes involving negative ions, such as detachment and transfer of electrons in collisions. Such a choice means that roughly we cover those aspects of negative ion chemistry that are related to thermodynamics and to astrophysics, the aspects that depend on equilibrium properties and on the interaction of isolated negative ions with radiation. The aspects we omit are those pertinent to gaseous discharge physics, to radiation damage problems, and to the study of ion–molecule reactions.

Our emphasis is primarily on assessing the state of our knowledge of the properties, of the level of precision and accuracy of this knowledge, and of how the information is obtained. At present, the larger part of our most accurate information about negative ions comes from experiments rather than from theory. Moreover, the theoretical methods for studying properties of these ions are essentially the same as those for studying neutrals or positive ions, while the experimental methods are considerably more specialized and sometimes almost unique. We therefore dwell considerably more on the experimental methods than on the theoretical, and in general simply cite the theoretical results and methods.

II. Electron Affinities

The most obvious and important quantity associated with a negative ion is the minimum energy required to detach its "extra" electron and form a neutral atom or molecule and an electron at rest very far away; this, of course, is the *electron affinity* of the corresponding neutral species. Among atomic properties, electron affinities have been just about the slowest to be determined with precision better than a few per cent, either experimentally or theoretically. In terms of experiments, precise and unambiguous electron affinity values have come from recently developed optical methods, although the largest number of affinities are still known from other procedures. For the theorist, electron affinities and other properties of negative ions pose greater difficulties than do properties of neutrals or positives, insofar as electron correlation plays a relatively larger part in determining the properties of a negative ion than it does in other species. In fact, electron affinities are frequently about the same size as the differences between correlation energies in atoms and in the corresponding negative ions.

The entire subject of negative ions including electron affinities was reviewed in detail by Massey in his monograph of 1950.[1] The most recent survey of electron affinities was that of Moiseiwitsch;[2] and Branscomb reviewed affinities in the context of photodetachment 3 years previously.[3] The best presently available electron affinities of atoms and small molecules are summarized in Table I. As a measure of the rapid development of the field, it is interesting to realize that every value in the table has been obtained since the time Massey's monograph appeared.

A. THE HYDRIDE ION

The primitive example of a negative ion is of course the hydride ion, H^-. We can obtain a rather good physical picture of this ion by examining its wave function. Let us use a function that allows for correlation, at least in part, by permitting the two electrons to be in different 1s orbitals. (The total function is antisymmetrized, of course.) From such a function, we can see that H^- is composed primarily of an electron bound weakly to the field of a polarized hydrogen atom, rather than having two simultaneously equivalent electrons, like a swollen $1s^2$ model of a helium atom. Figure 1 shows, in terms of radial wave functions, how this appears in the electron distributions. The figure is based on calculations of Roothaan and Weiss,[4] and specifically on that one of their wave functions which allows the electrons to be in different 1s orbitals but does not include the interelectronic distance explicitly. (They also consider more elaborate and accurate

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(1) H. S. W. Massey, "Negative Ions," 2nd ed, Cambridge University Press, London, 1950.

(2) B. Moiseiwitsch, *Advan. At. Mol. Phys.*, **1**, 61 (1965).

(3) L. M. Branscomb,"Atomic and Molecular Processes," D. R. Bates, Ed., Academic Press Inc., New York, N. Y., 1962, Chapter 4.

(4) C. C. J. Roothaan and A. W. Weiss, *Rev. Mod. Phys.*, **32**, 194 (1960).

Table I

Table of Electron Affinities

Atom	*Affinity,*[a] *eV*	*Ref*	*Atom*	*Affinity,*[a] *eV*	*Ref*
		A. Selected Values of Atomic Electron Affinities			
H	0.756 ± 0.13 (E)	Based on data of ref 6	Cl	3.613 ± 0.003 (E)	18
				3.616 ± 0.003 (E)	21a
	0.75415 (T)	5		3.56 (T)	67
Li	*Ca.* 0.6 (E)	35	K	>0.35, 0.49, or 0.75 (E)	66a
	0.62 (T)	64, 65		0.47 (T)	66
B	0.30 ± 0.06 (T)	65		0.902 ± 0.05 (T)	68
C	1.25 ± 0.03 (E)	11	Ti	0.391 ± 0.2 (T)	68
	1.17 ± 0.06 (T)	65	V	0.937 ± 0.025 (T)	68
	1.17 (T)	69a	Cr	0.980 ± 0.35	68
O	1.465 ± 0.005 (E)	10	Fe	0.582 ± 0.20	68
	1.478 ± 0.002 (E)	19	Co	0.936 ± 0.15	68
	1.22 ± 0.14 (T)	65	Ni	1.276 ± 0.20	68
	1.24 (T)	69a	Cu	1.801 ± 0.10	68
F	3.448 ± 0.005 (E)	18	Br	3.363 ± 0.003 (E)	18
	3.400 ± 0.002 (E)	21	Rb	>0.20 (E)	66a
	3.37 ± 0.08 (T)	65		0.42 (est)	66
	3.23 (T)	69a	Mo	1.0 ± 0.2 (E)	63a
Na	0.54 (T)	64	I	3.063 ± 0.003 (E)	18
Al	0.49 ± 0.14 (T)	65		3.076 ± 0.005 (E)	13
	0.52 (T)	67	Cs	>0.19 (E)	66a
Si	1.39 (T)	67		0.39 (est)	66
P	0.78 (T)	67	W	0.5 ± 0.3 (E)	63b
S	2.07 ± 0.07 (E)	12	Re	0.15 ± 0.1 (E)	63b
	2.12 (T)	67			
		B. Selected Values of Molecular Electron Affinities			
Molecule			*Molecule*		
OH	1.83 ± 0.04 (E)	15	NH_2	1.443 (E)	58
	1.91 (T)	73	HO_2	*Ca.* 3 (E)	*e*
SH	2.319 ± 0.010	15	C_3	1.8 (E)	*b*
	2.30 (E)	59	N_3	3.1 − 3.5 (E)	*f*
	2.25 (T)	73	NO_2(or NO_3?)	4.0 ± 0.2 (E)	63
SiH	1.46 ± 0.3 (T)	73b	SCN	2.16 ± 0.02 (E)	60
PH	0.93 ± 0.3 (T)	73b	SF_5	3.66 ± 0.04 (E)	62
C_2	3.1 (E)	*b*	SF_6	1.49 ± 0.02 (E)	62
CN	3.82 ± 0.02 (E)	*c*	C_6H_5	2.20 ± 0.05 (E)	61
NO	0.9 ± 0.1 (E)	63	$C_6H_5CH_2$	0.90 ± 0.08 (E)	61
O_2	0.15 ± 0.05 (E)	14			
	0.44 ± 0.02 (E)	*d*			

[a] All values are in eV; (E) means experimental and (T), theoretical. Only one experimental value is given except in a few cases chosen to illustrate the reliability of different methods, as indicated by their agreement (I, for example), or to illustrate discrepancies that now exist in the literature. [b] R. E. Honig, *J. Chem. Phys.*, **22**, 126 (1954); the author gives alternative values of 4.0 eV for C_2 and 2.5 eV for C_3, derived by a slightly different method. Honig stated that he felt the higher values were the more reliable. However, the affinity of 1.2 eV he gives for the C atom (his only value for this species) is quite accurate and is based on the same method he used to get the values cited in the table above; this is the reason for our own preference of the lower values for the affinities of C_2 and C_3. [c] J. Berkowitz, W. A. Chupka, and T. A. Walter, "Photoionization of HCN: the Electron Affinity and Heat of Formation of CN," to be published. [d] A. V. Phelps and J. L. Pack, *Phys. Rev. Lett.*, **6**, 111 (1961), from measurement of concentrations of negative ions produced by capture of thermal electrons by O_2. The value depends on the assumption of local equilibrium and of the nature of the capture reaction, namely $e + 2O_2 = O_2^- + O_2$. [e] H. O. Pritchard, *Chem. Rev.*, **52**, 529 (1953). [f] J. L. Franklin, V. H. Dibeler, R. M. Reese, and M. Krauss, *J. Am. Chem. Soc.*, **80**, 298 (1958).

functions, but these do not lend themselves to simple graphic representation.) Electronic polarization is just our simplifying way of describing electron correlation for relatively well-separated systems. Thus the wave function of H^-, represented approximately by the one-electron radial functions of Figure 1, is a reflection of the importance of correlation in negative ions.

Almost everything about the electron affinity of the hydrogen atom is atypical except its value. This number, 0.75415 eV, is by far the most accurately known electron affinity and was derived *a priori* from the elaborate theoretical calculations of Pekeris.[5] Second, the best experimental determination of the electron affinity of H comes not from a laboratory experiment but from the spectral properties of the star α-Tauri (Aldebaran). The balloon-borne spectrographic measurements reported by Woolf, Schwarzschild, and Rose[6] of the infrared spectrum of this star in particular (and of several other stars also, which give slightly less accurate results) clearly fixes a rather precise value for the photodetachment threshold. From the published spectrum, after the background is subtracted, we obtain a value of 1.64 ± 0.02 as the threshold wavelength and 0.756 ± 0.013 eV as the electron affinity of H^-. The best of other experimentally determined values is the

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(5) C. L. Pekeris, *Phys. Rev.*, 126, 1470 (1962).

(6) M. J. Woolf, M. Schwarzschild, and W. K. Rose, *Astrophys. J.*, 140, 833 (1964).

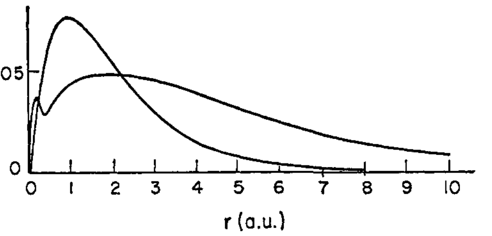

Figure 1. Radial wave functions for the electrons of H$^-$, based on the open-shell (1s1s′) calculation of ref 4. The calculation on which this figure is based was the most elaborate of those of ref 4 which did not include the electron–electron distance explicitly. The large difference between the sizes of the 1s and 1s′ radial functions and the similarity of the inner function to that of atomic hydrogen indicate the degree to which H$^-$ is qualitatively like an electron in the field of a polarized hydrogen atom.

theory-based extrapolation of Weisner and Armstrong[7] of the photodetachment cross sections measured by Smith and Burch;[8] the method of measurement is described in the next section. This procedure gives an affinity of 0.77 ± 0.02 eV for the hydrogen atom.

B. OPTICAL METHODS

Optical measurements of electron affinities stem ultimately from a suggestion that Franck made,[9] well before the era of quantum mechanics. Now, most of the accurately known electron affinities have been determined optically, by photodetachment or radiative capture. Two approaches have been used, principally, crossed beams and shock tubes; arc spectra also have been used to determine electron affinities.

The crossed-beam method developed at the National Bureau of Standards for the H$^-$ work just cited,[8] for the atomic ions of oxygen,[10] carbon,[11] sulfur,[12] and iodine,[13] and the molecular ions O_2^- [14] and OH$^-$,[15] makes use of a mass-selected beam of negative ions and a perpendicular beam of light. In most of the experiments, filtered light of known spectral composition was used, but recent work has utilized a monochromatic light beam of high intensity. A typical cross-beam photodetachment apparatus is shown schematically in Figure 2. The experimenter monitors the currents of negative ions and free electrons as functions of the light frequency and, to obtain extinction coefficients (cross sections) for photodetachment, the light intensity as well. The spectral range of the method is broad. On the low-energy side, crossed beams were used to determine directly the threshold for electron detachment from C$^-$. This threshold lies at 1.25 eV, meaning that wavelengths greater than 1 μ were used.[11] The highest energy example for which the crossed-beam method has been used is I$^-$; this requires only 3-eV radiation at threshold, but the study was carried out to 4 eV in order to detect all the significant features in the photodetachment cross section as a function of energy.[13]

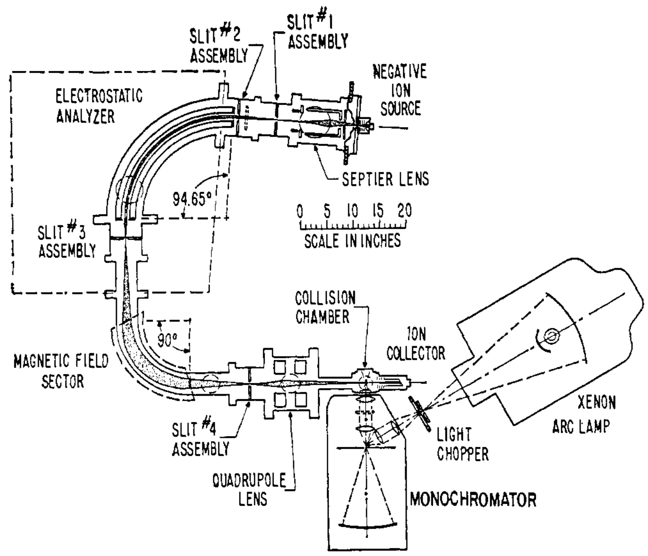

Figure 2. Schematic diagram of apparatus for crossed negative ion–photon beam studies of photodetachment. This diagram, of the most recent modification of the apparatus at the National Bureau of Standards, was very kindly supplied by Dr. Bruce Steiner.

The limitations of crossed-beam photodetachment are not severe; they are principally the requirement of an appropriate negative ion source, of high intensity in the light beam and of moderately stability in the two sources. Discharges have proved to be satisfactory sources; constricting the discharge electrically, magnetically, or both can be used to give large negative ion fluxes. A chopped-beam and phase-sensitive detection are normally employed in the crossed-beam method and currents are measured as such. Counting techniques have not been required for the determination just cited.

The second of the photodetachment techniques is one of direct spectroscopic observation. This is the method employed by this author and his associates to study Cl$^-$, Br$^-$, I$^-$, F$^-$, and O$^-$. The first four were observed initially in absorption;[16–18] oxygen was studied in emission,[19] using the inverse of photodetachment, radiative attachment. Spectroscopic observation requires that one prepare a sample with a sufficiently high concentration of the species of interest and that there be some way of making an unambiguous identification of the spectrum. In the case of the halide ions, a partially dissociated vapor of alkali halide molecules in equilibrium contains enough negative ions to permit their spectroscopic observation in a cell of reasonable length. Figure 3 shows a typical example of the concentrations of various species in CsBr vapor. The photodetachment cross sections are of order 10^{-17} cm^2. [Note that the photodetachment cross section σ_D (cm^2) = 3.824 × 10^{-21} ϵ (l./mole cm), in terms of the extinction coefficient ϵ.] Hence one may expect to observe photodetachment in the form of an absorption spectrum in an alkali halide vapor at a temperature of about 3000 °K, with about 10^{16} dissociated molecules/cm^3, in a cell about 10–50 cm long. The device actually employed to produce these conditions has been a shock tube. The salt is vaporized in a heat bath of shock-

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(7) J. D. Weisner and B. H. Armstrong, *Proc. Phys. Soc.*, **83**, 31 (1964).

(8) S. J. Smith and D. S. Burch, *Phys. Rev.*, **110**, 1125 (1959).

(9) J. Franck, *Z. Phys.*, **5**, 428 (1921).

(10) L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, *Phys. Rev.*, **111**, 504 (1958).

(11) M. L. Seman and L. M. Branscomb, *ibid.*, **125**, 1602 (1962).

(12) L. M. Branscomb and S. J. Smith, *J. Chem. Phys.*, **25**, 598 (1956).

(13) B. Steiner, M. L. Seman, and L. M. Branscomb, *ibid.*, **37**, 1200 (1962).

(14) D. S. Burch, S. J. Smith, and L. M. Branscomb, *Phys. Rev.*, **112**, 171 (1958); **114**, 1652 (1959).

(15) L. M. Branscomb, *ibid.*, **148**, 11 (1966). The SH$^-$ ion has also been studied very recently by B. Steiner, *J. Chem. Phys.*, **49**, 5097 (1968).

(16) R. S. Berry, C. W. Reimann, and G. N. Spokes, *ibid.*, **35**, 2237 (1961).

(17) R. S. Berry, C. W. Reimann, and G. N. Spokes, *ibid.*, **37**, 2278 (1962).

(18) R. S. Berry and C. W. Reimann, *ibid.*, **38**, 1540 (1963).

(19) R. S. Berry, J. C. Mackie, R. L. Taylor, and R. Lynch, *ibid.*, **43**, 3067 (1965).

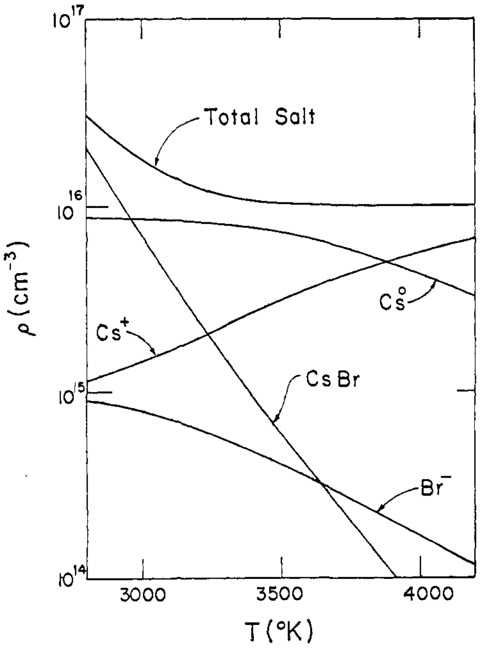

Figure 3. Concentrations of various species in CsBr vapor, as functions of temperature. The curves are drawn for the condition that total dissociated salt concentration is 10^{16} cm^{-3}. (The figure was taken from ref 76.)

heated argon. Spectra have been observed in both incident and reflected shocks. A flash lamp serves as the absorption source; the lamp is triggered, through a variable delay, by the shock wave's passage across a thermal resistance gauge. Spectra are recorded photographically on a conventional spectrograph.

The O^- poses a problem rather different from the halides, insofar as its equilibrium concentration is always very small. Therefore for O^-, shock-tube experiments were carried out a somewhat higher temperatures than with the halogens, and spectra were taken in emission, corresponding to the process

$$O + e \longrightarrow O^- + h\nu$$

This author and David observed emission thresholds for chlorine, bromine, and iodine in shock-heated alkali halide vapors.[20] Recently Popp[21,21a] has reported observations of the continuum due to electron capture by F atoms emitted from discharges in SF_6 and BF_3, and by Cl atoms in a discharge in Cl_2. With fluorine, Popp finds thresholds at 3646 ± 2 and 3595 ± 2 Å, corresponding to an electron affinity of 3.401 eV, in disagreement with the value of 3.448 ± 0.005 eV from the shock experiment. Presumably the threshold reported by Berry and Reimann at 3595 Å is the same as that found by Popp. The discrepancy arises from the question of whether this threshold is due to the production of $F(^2P_{1/2}) + e$, as Popp assigns it, or to the affinity threshold corresponding to the production of $F(^2P_{3/2}) + e$, as it was assigned by Berry and Reimann. The results are definitely inconsistent; in both cases, the authors claim to observe the two expected thresholds separated by an interval of 404 cm^{-1}.

In other cases, continuous spectra have been interpreted to contain significant contributions from radiative capture or photodetachment, but these spectra have not been used to determine thresholds. The first was Wildt's attribution of a "missing factor" in the infrared opacity of the sum to photodetachment from H^-.[22] We can trace a major stream in the study of negative ions from Wildt's work; it was followed by laboratory studies of luminosities of ionized gases in arcs and shocks in the Kiel laboratory of Lochte-Holtgreven, beginning with Lochte-Holtgreven's own study of H^- in arcs,[23] and by later work on H^- in arcs[24-28] and shocks,[29] and on O^-,[30] N^-,[31] and on Cl^-[32] in arcs. The existence of N^- was also inferred from optical measurements of shocks.[33] The astrophysical interest in photodetachment was one of the major stimuli, apparently, for the development of the crossed-beam method when the initial work was carried out on photodetachment from H^-.[8,34]

One recent use of continuous emission measurements was that of Ya'akobi.[35] He worked out the energy balance and observed the general shape of the continuous emission from an exploding lithium wire. From both of these, he inferred that soon (*ca.* 3 μsec) after the explosion, significant numbers of electrons were captured radiatively by neutral Li, and more quantitatively, that the threshold for this radiation, and therefore the electron affinity of lithium, is about 0.6 eV.

C. THRESHOLDS AND EXCITED STATES

Let us turn now to the identification of photodetachment and radiative capture spectra and to the assignment of the corresponding electronic states. Spectra of these types are obviously continuous and might at first consideration appear to pose severe identification problems. Fortunately, they are often as easy to identify as atomic lines. This is the case for the halogens and oxygen. Near the threshold energy, E_{thresh}, the photodetachment cross section σ_D varies with the energy of the incident light E according to

$$\sigma_D \propto (E - E_{\text{thresh}})^{l+1/2}$$

where l is the orbital angular momentum of the electron in its final, free state.[36] If one photodetaches an electron, the usual optical selection rule $\Delta l = \pm 1$ applies, so that if one photodetaches a p electron, this electron may leave its atom as a free s electron ($l = 0$). If $l = 0$, then σ_D is proportional to $(E - E_{\text{thresh}})^{1/2}$ and therefore has an infinite slope at threshold. Consequently, the continuum for photodetachment from O^- or a halide ion exhibits a sharp onset at the threshold energy, and the threshold shape of the continuous absorption cross section becomes a guide for identifying the continuum. A more positive identification can be made when more than one final state is available to the neutral atom product. With the

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(20) R. S. Berry and C. W. David in "Atomic Collision Processes" (Proceedings of the Third International Conference on Physics of Electronic and Atomic Collisions), M. R. C. McDowell, Ed., North Holland Publishing Co., Amsterdam, 1964, p 543.

(21) H.-P. Popp, *Z. Naturforsch.*, **20a**, 642 (1965); **22a**, 254 (1967).

(21a) G. Mück and H. P. Popp, *ibid.*, **23a**, 1213 (1968).

(22) R. Wildt, *Astrophys. J.*, **89**, 295 (1939).

(23) W. Lochte-Holtgreven, *Naturwissenschaften*, **38**, 258 (1951).

(24) R. Fuchs, *Z. Phys.*, **130**, 69 (1951).

(25) W. Lochte-Holtgreven and W. Nissen, *ibid.*, **133**, 124 (1952).

(26) Th. Peters, *ibid.*, **135**, 573 (1953).

(27) W. Nissen, *ibid.*, **139**, 638 (1954).

(28) A. Bohm and L. Rehder, *Z. Naturforsch.*, **20a**, 114 (1965).

(29) O. Weber, *Z. Phys.*, **152**, 281 (1958).

(30) G. Boldt, *ibid.*, **154**, 319 (1959).

(31) G. Boldt, *ibid.*, **154**, 330 (1959).

(32) H. Henning, *ibid.*, **169**, 467 (1962).

(33) R. A. Allen and A. Textoris, *J. Chem. Phys.*, **40**, 3445 (1964).

(34) L. M. Branscomb and S. J. Smith, *Phys. Rev.*, **98**, 1028 (1955).

(35) B. Ya'akobi, *Phys. Lett.*, **23**, 655 (1966).

(36) T. F. O'Malley, *Phys. Rev.*, **137**, A1668 (1965), and references therein.

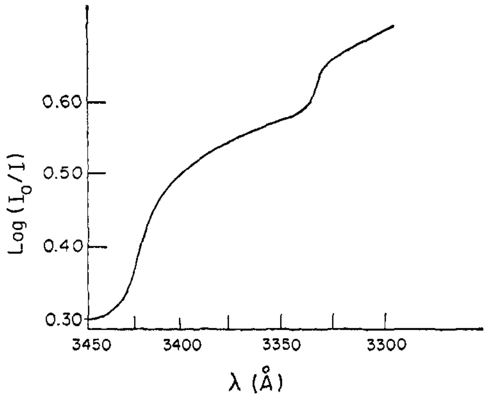

Figure 4. Typical photodetachment spectrum of Cl^- in the threshold region (based on the data of ref 17).

halogens, for example, the neutral atoms can be left in either their ground ${}^2P_{3/2}$ states or in excited ${}^2P_{1/2}$ states. The energy differences between these are well known from atomic spectra. Each of the possible final states gives rise to a threshold of its own. The energy interval between these thresholds is equal to the difference of the atomic state energies; the relative intensities of the cross sections originating at different thresholds are at least approximately in the same ratios as the statistical weights of the different transitions. The energy interval between thresholds is a particularly powerful quantity for making positive identifications of negative ions because of the precision with which it can be both predicted and measured. Fine structure splittings of this type have been used for identification of all the atomic halide negative ions and,[13,16–18] in emission, of the halides[20,21] and O^-.[19] However, as we noted in the previous section with reference to fluorine, even this method can have its uncertainties because of difficulties in analyzing weak spectral features. As an example of a straightforward case, the photodetachment spectrum of Cl^- in the threshold region is shown in Figure 4. The two thresholds, corresponding to the final ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states of Cl^0 are separated by 0.108 ± 0.007 eV; the fine structure splitting from the atomic spectrum of Cl is 0.1092 eV, in entirely satisfactory agreement. The uncertainty in the threshold measurement is due principally to the broadening of the spectrum at threshold by the random fluctuations in local electric fields in the partially ionized sample gas.

One feature of photodetachment spectra that was recently observed is detachment leaving the neutral in an electronically excited term or configuration. For example, detachment of a 2p electron from O^- may leave the neutral O atom in its metastable ${}^1D$ or ${}^1S$ state, rather than its ground ${}^3P$ state, provided the incident photon energy is greater than the corresponding threshold energy. These are 3.433 and 5.656 eV, respectively, compared with 1.465 eV for photoproduction of $O({}^3P)$ + e from O^-. The possibility of this process was discussed by Branscomb, Burch, Smith, and Geltman;[10] the recent measurements of Branscomb, Smith, and Tisone[37] have carried the cross-section data to energies of 4 eV; the ${}^1D$ threshold appears at 3.43 eV, as expected. This is potentially a way for producing a beam with a high concentration of excited neutral atoms, in the same way that photodetachment at lower energies applied to a negative ion beam, as described by Branscomb,[38] may be a powerful method for producing beams of fast ground-state atoms. If the electron being photodetached comes from any shell but the outermost, the negative ion is left in an excited *configuration*. For example, photodetachment of a 2s electron from O^- would produce an oxygen atom in its $2s2p^5$ configuration, in a ${}^1P$ or ${}^3P$ term. Such processes could be detected both by their absorption thresholds and in some cases by the emission of far-ultraviolet atomic lines, like the O atom lines at about 792, 575, and 641 Å, due to the 2p → 2s (${}^3P \rightarrow {}^3P$, ${}^1P \rightarrow {}^1D$, and ${}^1P \rightarrow {}^1S$) transitions. Relative intensities of these processes are presumably close to the values obtained by multiplying the atomic transition probabilities by the corresponding statistical weights of the excited atomic terms in the Russell–Saunders approximate forms for the negative ion excited term wave functions. Deviations from these intensities in light atoms might be useful guides for studying electron correlation in negative atomic ions.

Photodetachment spectra may contain "structure" not only because the neutral atom has more than one bound state. The negative ion may also have two or more states. Practically speaking, virtually all negative ions have only one bound electronic state. A large number of transient quasi-bound or even metastable states are now known and will be discussed in the final section; here, we examine only states whose energies are below the photodetachment threshold, and only later examine those lying in the continuum.

The C^- ion appears to have an excited state,[11] probably the ${}^2D$ corresponding to the first excited level of the isoelectronic N atom. This was inferred from the low photoelectron current from irradiation of a C^- beam at energies below the 1.2-eV photodetachment threshold for the ${}^4S$ ground state of C^-.

The O^- ion was occasionally suspected of having an excited electronic term, but it now seems clear that no such term exists. However, the ground ${}^2P$ term of O^- does have fine structure analogous to that of the fluorine atom, namely a ground ${}^2P_{3/2}$ state and an excited ${}^2P_{1/2}$ state. Fine structure in the threshold region of the radiative capture spectrum of oxygen atoms has been interpreted to be due in part to these two states, as well as to the fine structure in the neutral O atom.[19] From this interpretation, a value was derived of 190 ± 10 cm^{-1} for the spin–orbit coupling constant of the O^- ion, the only negative ion for which such a constant is now available. It should be pointed out that it is desirable that this constant be measured by some other independent method, because although the value is consistent with that of the isoelectronic F atom, it seems high by comparison with that of the neutral O atom.

Molecular negative ions may of course have many excited rotational and vibrational levels. When, as in OH^-, the extra electron is essentially nonbonding, the atomic and negative ion ground-state potential constants are very similar and the vibration–rotation levels of the ion are correspondingly like those of the neutral. When the extra electron is antibonding, as in O_2^- or a halogen negative ion molecule, or is bonding, as in CN^-, we can expect the potential curve of the ion to be, respectively, flatter and shifted to larger internuclear distances, or steeper and shifted to smaller internuclear distances. In

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(37) L. M. Branscomb, S. J. Smith, and G. Tisone, *J. Chem. Phys.*, **43**, 2906 (1965).

(38) L. M. Branscomb, private communication; B. Brehm, J. L. Hall, M. Gusinow, and L. M. Branscomb, 15th Annual Conference on Mass Spectrometry and Allied Topics, ASTM E-14, Denver, May 1967.

O_2^-, the equilibrium internuclear distance is almost 0.1 Å greater than the 1.207 Å of neutral O_2.[89]

Because the energy of a molecule or a molecular ion depends on internuclear distance, an important complication arises with molecular ions that does not occur with atoms. In the molecular case, we must distinguish between thermodynamic affinities (or ionization potentials or any other type of electronic transition, for that matter) and vertical processes. The thermodynamic affinity is based on the energies of molecule and molecular ion at their equilibrium positions.

$$EA_{\text{thermo}} = E[\text{AB}; R_e(\text{AB})] - E[\text{AB}^-; R_e(\text{AB}^-)]$$

Two vertical processes, processes occurring with essentially no change in internuclear distance, must be distinguished. One is the attachment of a zero-energy electron to the AB molecule when $R = R_e(\text{AB})$; the energy given up in this process is the vertical electron affinity of AB. The other process is the detachment of an electron from AB^- when $R = R_e(\text{AB}^-)$; the minimum energy required for this process is called the vertical detachment energy of AB^-. These processes are shown schematically in Figure 5.

In addition to the stable negative ion states we have been discussing, there are two other classes of negative ion states that have been of considerable interest lately. One class occurs when an extra electron responds to the attractive force of an excited atom or molecule. In effect, such states are negative ion states with two excited electrons. When these states cannot decay radiatively by an optically allowed transition, they are metastable and can frequently be detected by conventional methods. Those that can decay radiatively must be observed by indirect methods, usually by the resonances they produce in electron scattering on the corresponding neutrals. Electron-scattering resonances also betray the existence of some short-lived negative ion states in which no atomic electrons are excited. There are no metastable states for transients of this sort.

The most famous of the metastables is the He^- ion, first proposed by Hiby.[40] A lifetme of 18.2 ± 2.7 μsec was reported recently[41] for metastable He^-, presumably in its 1s2s2p, $^4P_{5/2}$ state, determined by a time-of-flight measurement. By analyzing the energy of photodetached electrons, Brehm, Gusinow, and Hall[42] have determined the electron affinity of the 2^3S state of helium as 0.080 ± 0.002 eV. Their method utilized an argon-ion laser as the light source rather than the energy selected light used in the crossed-beam experiments we discussed previously; the authors point out that their procedure seems to open the possibility of determining electron affinities from other metastable or relatively weakly bound negative ions.

We shall not attempt to cover the subject of electron-scattering resonances and the corresponding negative ions. At the end of this article we cite bibliographies of the recent literature in the field. The classification and analysis of these states has proved to be a fruitful ground for theoretical study, as several recent investigations have demonstrated.[43-48]

One situation peculiar to molecules arises when the negative ion molecule is truly stable for large values of the internuclear distance but becomes unstable relative to the free electron plus neutral molecule if the internuclear distance is small. This situation arises in H_2^- and is discussed later in the context of theoretical studies.

D. OTHER EXPERIMENTAL METHODS

An interesting method for determining the electron affinity of the oxygen atom was performed by Schulz[49] and interpreted by Chantry and Schulz[50] in a way that illuminates an important effect for many fragmentation processes caused by electron impact. The method requires that one produce $O^- + O$ from electron capture by O_2, and measure the kinetic energy of the O^- as a function of electron energy. (This procedure demands high-energy resolution in the electron source.) One then essentially extrapolates to find the electron energy which would produce O^- with zero kinetic energy. Chantry and Schulz showed, with a very elementary argument, that if one simply makes a linear extrapolation, the thermal velocity of the O_2 target molecules can lead to an apparent value of the electron affinity that is very much in error, even though the thermal energy may be low compared with the recoil energy of the dissociation products. With full account taken for the thermal velocity of the target, the affinity given by this method is 1.5 eV, in quite satisfactory agreement with the more precise values from photodetachment and radiative capture. Without considering the motion of the O_2, one would obtain 2.0 eV.

Still another method is illustrated in the photodissociation method of Elder, Villarejo, and Inghram.[51] They produced $O^+ + O^-$ by photodissociation of O_2; by measuring $h\nu_0$, the threshold energy of the photons, estimating from the efficiency function the kinetic energy of the ions, T, and knowing the dissociation energy of O_2, $D_e(O_2)$, and the ionization potential of O, $I(O)$, the electron affinity is determined.

$$A = D_e(O_2) + I(O) + T - h\nu_0$$

The method gives a value of 1.461 ± 0.024 eV for the electron affinity of the oxygen atom, again consistent with the photodetachment value.

Among other experimental methods for determining electron affinities are (a) inference from thermodynamic and especially lattice energy calculation, (b) electron impact, *e.g.*, to form $C^+ + O^-$ by electron collisions with CO, (c) measurement of the equilibrium concentration of negative ions in a gas of known temperature and composition, particularly of C^- in carbon vapor, and, most important, (d) surface ionization. All of these except the last were adequately reviewed by Moiseiwitsch[2] and require no further comment

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here. Surface ionization was one of the first general methods for producing negative ions and measuring electron affinities. Mayer and his associates[52–55] developed the method for studying the halogen atoms. The experimental method was refined and the data were analyzed in a more elaborate way by Page and his coworkers[56–63] to take into account specific surface processes, and used by them to study a considerable number of molecular electron affinities as well as those of the halogens and oxygen and sulfur atoms. The method is essentially thermodynamic; without elaborating on the refinements, one measures the filament temperature and the concentrations (as currents) of electrons and total negative ions. Among the molecular ions studied by this procedure are NH_2^-, SH^-, CN^-, SCN^-, $C_6H_5^-$, $C_6H_5CH_2^-$, SF_6^-, SF_5^-, and tetracyanoethylene. The method will be still more powerful and the interpretations in complex systems will be more straightforward and certain when, as Page has pointed out, a mass spectrometer is used to monitor the negative ions. As it has been used, ambiguities may occur, as, for example, between NO_2^- and NO_3^-.

Very recently, Scheer and Fine have used a method closely related to the surface ionization method of Mayer and Page to obtain an electron affinity for Mo[64] and estimates for the affinities of W and Re.[65] Specifically, they have measured, with a mass spectrometer, the flux of atomic ions evaporating from an incandescent filament. By measuring the temperature dependence of the fluxes of positive and negative ions j_+ and j_-, respectively, they were able to evaluate the electron affinities A in terms of the work function ϕ of the metal, the sublimation energies l_0^T and l_+^T of the free atoms and positive ions, respectively, and the partition functions ω_+ and ω_- for the free ions.

$$A = \phi + l_0^T - l_+^T kT \ln [(\omega_-/\omega_+)(j_+/j_-)]$$

The method is restricted to a temperature range low enough that the negative space charge does not inhibit negative ion collection and the positive ion flux is low enough to permit accurate counting. The uncertainties lie in the degree to which the vapor and metal surface are in thermal equilibrium, and in the accuracies with which the values of ϕ, l_0^T, and l_+^T are known.

Still another method based on electron capture yields lower bounds for electron affinities. This is photosensitized ionization, which Lee and Mahan recently used to study vapors of K, Rb, and Cs. Specifically, they irradiated alkali vapors with monochromatic light of variable wavelength and monitored the currents produced by light of wavelength longer than that at the alkali atomic photoionization thresholds. They were able to attribute part of the ionization to processes of the types

$$M^* + M \longrightarrow M_2^+ + e \text{ (associated ionization)}$$

and

$$M^* + M \longrightarrow M^+ + M^-$$

By assuming that the molecule ions are more mobile than the atomic ions (because the atomic ions exchange charge readily with neutral atoms), Lee and Mahan were able to attribute a specific low-energy limit to the onset of the second process and, thereby, to set lower limits for the electron affinities of K, Rb, and Cs.

E. THEORETICAL DETERMINATIONS

Theoretical electron affinities of atoms in their ground states can be computed with chemically useful accuracy. The H^- affinity is of course better determined from theory than from experiment, as discussed earlier in this section; the calculations by Pekeris[5] are some of the most extensive ever undertaken in atomic computational studies. The affinities of the alkalis Li, Na, and K have been studied by Weiss,[66] who used the method of configuration interaction, so that the wave functions would include the very important effects of correlation. For lithium, Weiss derived an affinity of 0.62 eV, in excellent agreement with the experimental vaue of 0.6 eV.[35] No definitive experimental determinations have been made for sodium and potassium; the theoretical affinities are 0.54 and 0.47 eV, respectively. Weiss also examined the possibility of Be^- and Mg^- ions and found no evidence for their stability. A large number of atomic electron affinities have now been computed by Clementi and his collaborators,[67–69] with a method which includes an approximate correction to the Hartree–Fock expression to account for electron correlation. By and large, the values obtained this way have been within about 15% or better of the experimental values and can be considered reliable guides for purposes. The theoretical values are generally lower than the experimental, implying that the Hartree–Fock energies of the atoms are closer to the exact values than are those of the negative ions, or that the correlation corrections are usually too small. The electron pair correlations dominate the effects of correlation. This can be seen from the accuracy of the affinities of C, O, and F calculated very recently by Sinanoglu and Öksüz[69a] with a method that includes the Hartree–Fock mean field and pair correlation contributions quite accurately and neglects higher order correlations. A number of extrapolation methods have been proposed and are reviewed by Moiseiwitsch. However, in view of the quality of the calculations by Clementi and McLean,[67] by Clementi,[68] and by Clementi, McLean, Raimondi, and Yoshimine,[69] the extrapolation methods can now be considered superseded.

Calculations of electron affinities have been carried out for a few molecules. For H_2^-, Taylor and Harris[70] derived a quite accurate potential curve that lies below the H_2 curve for internuclear distances greater than 3 au; at smaller distances,

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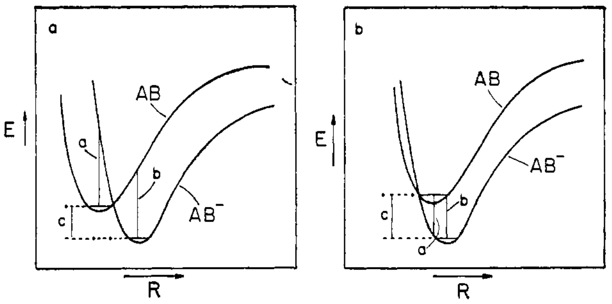

Figure 5. Vertical electron affinities (a), vertical detachment energies (b), and thermodynamic electron affinities (c) for two possible cases: (5a) vertical affinity negative, thermodynamic affinity and vertical detachment energy positive, as in (theoretical) Cl_2 case; (5b) all three quantities positive, as in (theoretical) Br_2 and I_2 cases.

the H_2^- curve would lie above the curve for H_2 + e, so that H_2^- becomes unstable. This instability can be treated as a problem of finding the energy width of a transient state. It can be considered in terms of collision processes of H and H^- or of electrons on H_2, and will be discussed briefly in the following section.

The affinities of halogen diatomics have been treated both as *a priori* problems, by Wahl and Gilbert,[71] and as semiempirical problems, by Person.[72] As in all problems of molecular electron affinities, the electron affinity of a halogen molecule is a function of internuclear distance. Like O_2 and O_2^-, the neutral halogen molecules are smaller and stiffer than their negative ion counterparts. The equilibrium point on the neutral Cl_2 curve lies below the Cl_2^- "curve," according to the calculations of Wahl and Gilbert. (We use quotation marks because the negative ion is not really stable and does not really have a sharply defined curve whenever its potential energy lies above that of the neutral molecule, *i.e.*, in the continuum of AB + e.) This situation is shown in Figure 5a. According to Person, the potential curves for Br_2^- and I_2^- lie below the corresponding neutral curves at R_e of the neutrals, as in the situation of Figure 5b. In the former case, the vertical affinity is negative, while the thermodynamic affinity and vertical detachment energies are positive. In the latter case, all three quantities are positive.

The OH^-, CH^-, SiH^-, SH^-, and PH^- ions have been studied theoretically by Cade,[73] in a series of Hartree–Fock calculations. The spectroscopic and potential constants from these calculations for the ions are in excellent accord with those of the corresponding OH and SH calculated also with Hartree–Fock functions. These findings, albeit not based on exact functions, are quite consistent with the experimental findings for OH^-.[15] Essentially, the extra electron of the ion is almost completely nonbonding.

III. Cross Sections for Photodetachment

The photodetachment cross section is, in effect, a product of a transition dipole strength and a density of continuum states. The transition dipole is generally a smooth and gradually varying function, so that in regions near thresholds, the shape of the curve of photodetachment cross sections *vs.* energy is fixed by the density of states that can be reached by electric dipole transitions, while the over-all height or vertical scale is fixed by the transition matrix element. The state density is responsible for the relationship $\sigma_D \propto (E - E_{\text{thresh}})^{l+1/2}$, and the constant of proportionality contains the squared modulus of a transition dipole. In contrast to photoionization, the final state in photodetachment consists of an electron interacting with a weak and short-range potential. The short range of the potential keeps it from giving large accelerations to nearby electrons; hence the velocity, and therefore the angular momentum, of a low-energy electron close to an atom is most likely to be low. That is to say that the density of low-energy states with large amplitudes near an atom must be low except for states of very low angular momentum. This qualitative description is in essence the origin of the l dependence of the photodetachment cross section near threshold. It is possible to develop a formal series representation in $(E - E_{\text{thresh}})$ for photodetachment,[10,38] in the threshold region. The terms of the series depend on the atomic parameters of polarizability and quadrupole moment. However, no one has yet derived atomic parameters from the shapes of photodetachment cross-section curves.

A. ATOMS

Relative photodetachment cross sections, *i.e.*, the extinction coefficients as functions of incident light frequency, are rather straightforwardly obtained from both crossed-beam and spectroscopic measurements, at least in principle. Both methods have some inherent experimental difficulties that complicate even the relative measurements. For example, in the beam method, Steiner[74] has pointed out the problems of differences in sensitivity of different parts of a detector surface. In the spectroscopic method, where, originally, relatively high ion densities were used, careful studies of threshold shapes showed that the apparent cross-section curves sometimes exhibited inflections and even maxima.[75] Furthermore, the sizes of these anomalies were functions of the densities of alkali halide in the gas. Later measurements made with much lower densities show no such anomalies.[76]

Despite the drawbacks, relative cross sections have been measured for H^-, O^-, C^-, I^-, OH^-, and OD^- by the beam method and in the threshold regions for the halides and for O^- by the spectroscopic approach.

Absolute intensities or cross sections are more difficult to measure, of course. These fall in the range 10^{-17}–10^{-18} cm^2, large enough that low intensities are not a predominant major obstacle; for example, Steiner[74] has been able to measure the absolute photodetachment cross section of I^- by amplifying the current of photodetached electrons and has not had to use counting methods. Uncertainties in absolute cross sections arise at present from several causes; uncertainties in primary standards, when "absolute" cross sections are determined relative to another standard, and uncertainties in the density of negative ion absorbers are probably the two major sources of uncertainty now.

In the case of H^-, an absolute photodetachment cross section was derived experimentally from the measured relative cross section as a function of energy,[8] and the absolute value

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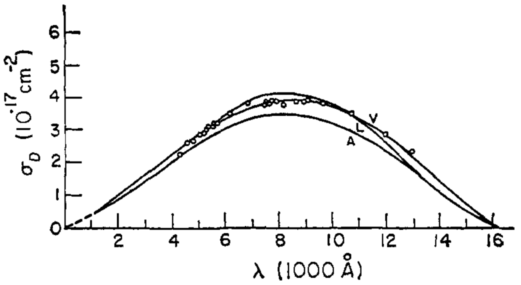

Figure 6. Photodetachment spectrum of H^- from theory and experiment. The points are based on the data of ref 8; the curves, on ref 77. L indicates the dipole length method; V, dipole velocity, and A, dipole acceleration.

of various integrals of this cross section derived from experiments with broad-spectrum light sources.[84] This experimental cross section is in good agreement with recent theoretically derived curves.[77–79] The theoretical curves are themselves in fairly close agreement. The photodetachment cross section of H^- has traditionally been the main proving ground for one of the most stringent probes of the quality of wave functions, namely for the comparison of the dipole length, dipole velocity, and dipole acceleration expressions of the transition probability. These three forms are[78]

$$\sigma_L = 6.812 \times 10^{-20} k(k^2 + 2A) \left| \langle F | \Sigma Z_i | B \rangle \right|^2 \text{ cm}^2$$

$$\sigma_V = 2.725 \times 10^{-19} \frac{k}{(k^2 + 2A)} \left| \left\langle F \middle| \Sigma \frac{\partial}{\partial Z_i} \middle| B \right\rangle \right|^2 \text{ cm}^2$$

$$\sigma_A = 1.090 \times 10^{-18} \frac{k}{(k^2 + 2A)^3} \left| \left\langle F \middle| \Sigma \frac{Z_i}{\gamma_i^3} \middle| B \right\rangle \right|^2 \text{ cm}^2$$

where k is the wave number of the detached electron (in a_0^{-1} or bohr^{-1}), A is the electron affinity (in e^2/a_0 or Hartree atomic units), the wave functions $|F\rangle$ and $|B\rangle$ represent free and bound states for the entire system, and the sums are over all electrons. For exact wave functions, these three expressions must be equivalent; the equivalence can be derived by using commutator identities such as $[q,\mathcal{H}] = i\hbar(2m)^{-1}p$, and by assuming that one's wave functions are exact eigenfunctions of $\mathcal{H}$, so that $\mathcal{H}|F\rangle = E_F|F\rangle$ and $\mathcal{H}|B\rangle = E_B|B\rangle$. The deviations of the functions one actually uses from the true wave functions appear in the guise of unequal values for σ_L, σ_V, and σ_A. Figure 6 shows the photodetachment cross section of H^- as determined by Doughty, Fraser, and McEachran,[77] and by the experiments of Smith and Burch.[8]

Cross sections for O^- from theory and experiment are in good accord, up to the threshold for the appearance of $O(^1D)$ + e. Beyond this point, the theoretical curves[80,81] are roughly 50% higher than the experimental curve of Branscomb, Smith, and Tisone;[37] the experimental points in the highest energy region, however, may be subject to considerable uncertainty, according to the authors. Essentially, the curve rises in the first 0.4 eV from threshold to approximately 7×10^{-18} cm^2, and is approximately constant up to the threshold at 3.4 eV. The detailed threshold shape was studied in the emission (radiative capture) spectrum.[19]

The cross section for I^- was determined on a relative scale by the crossed-beam method by Steiner, Seman, and Branscomb,[82] and was recently fixed to an absolute value by Steiner[74] by comparing the cross section for I^- with that of H^-, at energies 0.5 eV above the corresponding thresholds. This method was chosen in order to compensate for chromatic aberrations in the electron-collecting system. Thus $\sigma_D(H^-)$ at 9930 Å was compared with that of $\sigma_D(I^-)$ at 3470 Å. The value of $2.9 \pm 0.4 \times 10^{-17}$ cm^2 was obtained for the latter of these quantities and is approximately the value of σ_D over most the range up to the threshold for production of $I(^2P_{1/2} + e)$.

Approximate absolute values for the atomic halide ion photodetachment cross sections were derived from the spectroscopic measurements,[17,18] with the assumption that the systems were in local thermal equilibrium. Detailed relation shapes of these cross sections in their threshold regions were obtained at the same time. More recently, Berry, Cernoch, Coplan, and Ewing[76] have established an absolute cross section for $\sigma_D(Br^-)$ by establishing that the system is in thermal equilibrium, and then by comparing the Br^- extinction with that of a cesium line of moderately well-known oscillator strength. The value of $\sigma_D(Br^-)$ at 3637 Å obtained this way is $2.5 \pm 0.6 \times 10^{-17}$ cm^2, of the same magnitude as $\sigma_D(I^-)$. The Cl^- cross section seems to be similar, but that of F^- is somewhat smaller.

Rothe[82a] has very recently determined cross sections for Cl^-, Br^-, and I^- from radiactive capture of electrons by halogen atoms, in shock-heated vapors of sodium halides in argon. The values obtained this way are in good agreement with previously determined ones,[17,18,82] but are somewhat lower than that for Br^- reported by Berry, Cernoch, Coplan, and Ewing.[76] The latter, however, depends on a rather poorly known oscillator strength and may well need revision.

The cross section for C^- was studied experimentally by Seman and Branscomb,[11] and theoretically by Robinson and Geltman,[80] by Myerscough and McDowell,[83] and by Cooper and Martin[84] who also treated O^-, F^-, and Cl^-. The agreement of theory and experiment in the case of carbon is not as good as for oxygen, particularly with regard to the threshold shape. The theoretical curves rise less rapidly from threshold than does the experimental curve. If the experimental points are correct and no systematic errors have been overlooked, then the real neutral carbon atom would appear to have a more attractive interaction with a free, low-energy electron than the theories admit, even though the theories take at least partial account of exchange and polarization interactions between the free and bound electrons.

B. DIATOMIC MOLECULES

The molecular ions for which photodetachment cross sections have been published, OH^- (and OD^-), SH^-, and O_2^-, are very different from each other. The hydroxide[15] ion looks much like a first-row atomic ion; $\sigma_D(OH^-)$ rises rapidly at about 7000 Å to a plateau, with a height of *ca.* 10^{-18} cm^2 between 6500 and 4000 Å. The observed OH^- and OD^- spectra are attributed to the (0, 0) transitions, with a possible suggestion of a (1, 0) transition to $v = 1$ of OH from $v = 0$

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of OH^-. That the OH^- and OD^- curves are superimposable and show no isotope shift shows that the vibrational frequencies of the neutral and corresponding ionic molecules are approximately equal.

The O_2^- molecule ion is quite different from OH^-; the O_2^- potential minimum is shifted to an internuclear distance almost 0.1 Å larger than that of the ground state of neutral O_2.[39] Consequently the photodetachment cross section contains contributions from many vibrational states of the neutral and shows no sharp threshold. Rather, the observed cross section rises slowly from 3.5×10^{-20} cm² at 0.15 eV to 2.39×10^{-13} cm² at 2.94 eV. Another factor making $\sigma_D(O_2^-)$ small near threshold is that the most easily detached electron leaves from a *gerade* π orbital, so it cannot make an optical transition into a *gerade* s wave. Geltman has shown[85] how photodetachment cross sections of molecules behave near threshold, and in particular, that one should expect $\sigma_D(O_2^-)$ to vary as $(E - E_{\text{thresh}})^{3/2}$, consonant with the experimental data.[10] It is not possible to determine unambiguously the various contributions to the shape of the curve for $\sigma_D(O_2^-)$: the threshold behavior, the transitions for internuclear distances $R \neq R_e$, and transitions from excited vibrational states. Consequently the "vertical" electron affinity, *i.e.*, the energy difference between O_2 + e and O_2^- at $R_e(O_2^-)$, is not well established.

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IV. Further References

In addition to the articles and books cited in the footnotes, other source materials deserve special mention here. These are the following bibliographic compilations: "Atomic and Molecular Collision Cross Sections of Interest in Controlled Thermonuclear Research,"[86] and the subsequent "Bibliography of Atomic and Molecular Processes,"[87] produced semiannually by the Atomic and Molecular Processes Information Center (AMPIC), and "Bibliography of Low Energy Electron Collision Cross Section Data,"[88] produced at the Joint Institute for Laboratory Astrophysics. The last of these is intended also to be a serial publication.

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(86) C. F. Barnett, J. A. Ray, and J. C. Thompson, "Atomic and Molecular Collision Cross Sections of Interest in Controlled Thermonuclear Research," ORNL-3113 Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964; available from the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.

(87) "Bibliography of Atomic and Molecular Collision Processes," compiled by the Atomic and Molecular Processes Information Center (AMPIC), C. F. Barnett, Director, Oak Ridge National Laboratory, Oak Ridge, Tenn., issued semiannually; available from the Clearinghouse for Federal Scientific and Technical Information, the National Bureau of Standards, U. S. Department of Commerce, Springfield, Va. 22151.

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