

## Electron affinities of Cu and Ag\*

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(Received 6 November 1972)

In a crossed-beam experiment, photodetachment of  $\text{Cu}^-$  and  $\text{Ag}^-$  ions by an Ar-ion laser beam (4880 Å) is studied by energy analyzing the detached electrons. The electron affinities are found to be: E.A. (Cu) =  $(1.226 \pm 0.010)$  eV, E.A. (Ag) =  $(1.303^{+0.007}_{-0.011})$  eV. These electron affinities are approximately 0.5 eV less than those determined by surface ionization studies. The surface ionization technique is discussed and possible reasons for the discrepancies are advanced. The new electron affinities are used to estimate those of the atoms in the long series of the periodic table. Measurements of the angular distribution of the photo-detached electrons yield  $\beta = 2.00 \pm 0.03$  for the anisotropy parameter  $\beta$  in both cases.

### I. INTRODUCTION

The electron affinity (E.A.) of atoms is an important quantity in many aspects,<sup>1-7</sup> yet to date accurate data (accurate to within 10–20 meV) are available only for about a dozen atoms,<sup>7</sup> including the halogens, H, C, O, S,<sup>8</sup> and Se.<sup>9</sup> Very recently, Hotop and Lineberger<sup>10</sup> have reported the precise determination of the electron affinities of Au and Pt in a dye laser photodetachment experiment; in the case of Ag, they established 1.78 eV as an upper bound for its E.A.

The surface ionization technique<sup>5,11</sup> has been used earlier in a number of different approaches<sup>12-14</sup> to obtain E.A.'s for Cu, Ag, and Au, which are particularly interesting candidates outside the main group elements of the periodic table. These are the closing elements of the three long series ( $\text{K} \rightarrow \text{Cu}$ ,  $\text{Rb} \rightarrow \text{Ag}$ ,  $\text{Cs} \rightarrow \text{Au}$ ), and it would be useful to have accurate EA values to use in isoelectronic extrapolation (IE) work<sup>15,16</sup> thus providing reliable "benchmarks" on this side of the long series. Bakulina and Ionov<sup>12</sup> obtained the following values in a relative surface ionization experiment (relative to iodine atoms): E.A.(Cu) =  $(1.5 \pm 0.5)$  eV, E.A.(Ag) =  $(2.0 \pm 0.2)$  eV, E.A.(Au) =  $(2.8 \pm 0.1)$  eV. These numbers were actually used by Zollweg<sup>16</sup> in his horizontal IE analysis to estimate the electron affinities of the elements in the long series. Zandberg and colleagues<sup>13</sup> have measured E.A.(Ag) absolutely via surface ionization and obtained  $(1.90 \pm 0.15)$  eV, and, in a relative measurement,<sup>14</sup> they determined E.A.(Cu) = E.A.(Ag) - 0.12 eV (+0.06 eV).

The photodetachment result<sup>10</sup> for Au [ $(2.3086 \pm 0.0007)$  eV] casts some doubt on the validity of even a relative determination of an electron affinity in surface ionization experiments, and the behavior of the photodetachment cross section of  $\text{Ag}^-$  in the range  $1.78 \text{ eV} < h\nu < 2.2 \text{ eV}$  suggested that E.A.(Ag)  $\lesssim 1.5$  eV, again in disagreement with the surface ionization result.

In the present paper, we report on direct and unambiguous determinations of the electron affinities

of Cu and Ag atoms in a laser (4880 Å) photodetachment experiment.<sup>17</sup> In this experiment the detached electrons are energy-analyzed and their energy is determined relative to that of electrons which have been detached simultaneously from negative ions with known electron affinities.

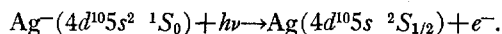
### II. EXPERIMENTAL

The technique used here has been previously described in detail.<sup>17</sup> Briefly, a 680 eV beam of negative ions is illuminated by the linearly polarized intracavity field of an argon-ion laser (4880 Å). Those electrons, which are photodetached into the acceptance angle  $[(4\pi/2000)sr]$  of a hemispherical electrostatic condenser, are energy analyzed ( $\Delta E \approx 50$  meV) and detected. The ion beam, laser beam, and electron collection directions are mutually orthogonal. The rotation of the laser polarization direction by means of a half-wave plate allows us to measure photodetachment electron angular distributions.

Negative ion beams of about 0.3 nA  $\text{Ag}^-$  or  $\text{Cu}^-$  are produced in a sputter ion source<sup>10</sup> run with suitable mixtures of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NH}_3$ . Mass analysis is performed in a Wien filter.

### III. RESULTS AND DATA ANALYSIS

The energy spectrum of electrons photodetached from an  $\text{Ag}^-$  beam<sup>18</sup> is shown in Fig. 1. Figure 1(b) gives the data obtained with the electric vector of the laser light close to parallel to the sampling direction ("vertical polarization"). Figure 1(a) shows the other extreme case of "horizontal polarization." In both cases, only one peak is observed, corresponding to the transition



A strong preference is seen for ejection of the electrons along the electric vector [note the different ordinates in 1(a) and 1(b)].

The angular distribution of photoelectrons has the

TABLE I. Electron affinities of Cu, Ag, and Au in electron volts.

Author	Reference	Method	Cu	Ag	Au
Bakulina, Ionov	12	Relative surface ionization	$1.5 \pm 0.5$	$2.0 \pm 0.2$	$2.8 \pm 0.1$
Zandberg <i>et al.</i>	13	Absolute surface ionization	...	$1.90 \pm 0.15$	...
Zandberg <i>et al.</i>	14	Relative surface ionization	E.A.(Ag) $-0.12 \pm 0.06$	...	...
Hotop, Lineberger	10	Photodetachment	...	$\approx 1.5$ $+0.007$	$2.3086 \pm 0.0007$
This work		Photodetached electron spectroscopy	$1.226 \pm 0.010$	$1.303$ $-0.011$	...
Clementi	21	Hartree-Fock calculation	$1.80 \pm 0.1$	...	...
Schwarz	22	Pseudopotential calculation	0.7	...	...
Charkin, Dyatkina	15	Isoelectronic extrapolation	1.4	1.5	...

general form (for dipole transitions)<sup>19</sup>

$$I(\theta) = C[1 + \beta P_2(\cos \theta)], \quad (1)$$

where  $\theta$  = angle between electric vector of light and electron collection direction. The anisotropy parameter  $\beta$  is limited theoretically to the range  $-1 \leq \beta \leq 2$ . Experimentally, it was found that  $\beta = 2.00 \pm 0.03$  for detachment from both  $\text{Cu}^-$  and  $\text{Ag}^-$  at  $\lambda = 4880 \text{ \AA}$  (2.45 eV), after correction was made for the depolarization of the laser light ( $\approx 1\%$ ) and the finite solid angle for electron collection.

The electron spectrum for  $\text{Cu}^-$  detachment<sup>20</sup> was essentially the same as for  $\text{Ag}^-$ , except for the difference in the energy location of the peak observed.

In order to determine the electron affinity of Cu and Ag, electrons resulting from photodetachment of  $\text{Cu}^-$  ( $\text{Ag}^-$ ) and  $\text{OH}^-$  ( $\text{O}^-$ ) ions were measured at the same time by electrically switching the Wien filter back and forth to the masses of the ions under study. This was done at a number of different directions of the polarization of the laser light.

The center of all the electron peaks for  $\text{Cu}^-$ ,  $\text{Ag}^-$ ,  $\text{O}^-$ , and  $\text{OH}^-$  detachment (which leads to a single peak in each case at the present resolution of the electron analyzer) was determined accurately (to  $\pm 3 \text{ meV}$  or better) by a computer fit to the data.<sup>17b</sup> These fits, together with the known corrections for the mass-dependent kinematic energy shifts, provide a direct measurement of the energy difference between the centroids of the detached electron peaks of the ion under study and the reference ion.

Using an effective electron affinity of 1.465 eV for O and 1.829 eV for OH (which corresponds to the center of the observed electron peaks in both cases, as explained in the appendix) we obtain

$$\begin{aligned} \text{E.A.}(\text{Cu}) &= (1.226 \pm 0.010) \text{ eV} \\ \text{E.A.}(\text{Ag}) &= \begin{pmatrix} +0.007 \\ 1.303 \\ -0.011 \end{pmatrix} \text{ eV.} \end{aligned}$$

The error limits include the uncertainty in the location of the  $\text{O}^-$  and  $\text{OH}^-$  peaks (see appendix), systematic errors from the energy-scale calibration,<sup>17b</sup> and reflect the reproducibility of the data over different runs.

#### IV. DISCUSSION AND CONCLUSIONS

Table I summarizes the results obtained in the present work together with other experimental<sup>12-14</sup> and theoretical values.<sup>15,21,22</sup> For completeness, we have added the values for Au.<sup>10,12</sup> It is seen that the surface

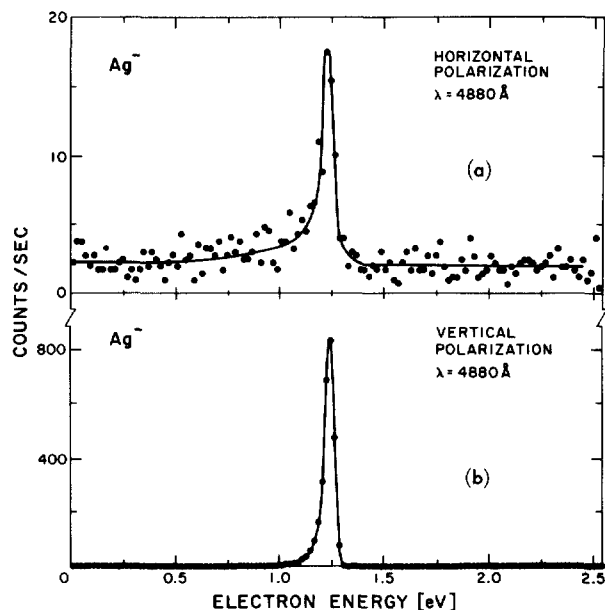


FIG. 1. Energy spectra of electrons detached with Ar ion laser light  $\lambda = 4880 \text{ \AA}$  (2.540 eV) from a 680 eV  $\text{Ag}^-$  beam. The highly anisotropic angular distribution is apparent from the difference in the scales of the ordinates even though the integration time was a factor of 2 greater in (a): (a) polarization of light horizontal, i.e., the electric vector of the laser light is perpendicular to the electron sampling direction. (b) polarization of light vertical, i.e., the electric vector is parallel to the electron sampling direction.

ionization (SI) results are about 0.5 eV too high in all cases. It is not easy to judge why the SI electron affinities are so different from our results. Apparently, some of the assumptions made in the evaluation of the SI data are not fulfilled. We briefly describe the methods used in the SI work related to Table I.

Bakulina and Ionov<sup>12</sup> measured the ratio of negative ion currents  $i_1/i_2$ , coming from a heated metal surface on simultaneous impact of beams of two different atoms 1, 2 (the electron affinity E.A. of one of which is known) as a function of the temperature of the metal surface  $T$ . The slope of the graph  $\ln(i_1/i_2) = f(1/T)$  gives the difference E.A.(1) - E.A.(2) of their electron affinities. This method is considered<sup>5</sup> to be one of the best SI methods for the determination of E.A.'s. Bakulina and Ionov<sup>12</sup> measured the E.A.'s of Cu, Ag, and Au relative to that for I in this way.

Zandberg and colleagues<sup>13,14</sup> take a somewhat different approach. They measure the ratios of negative to positive ion currents coming from a hot metal surface (e.g., tungsten wire) at a certain temperature  $T$ , when two different atomic beams of species 1, 2 impinge simultaneously on the surface. Thus they determine the quantity  $E.A.(1) - E.A.(2) + V_1 - V_2$ , where  $V_i$  are the (known) ionization potentials of 1 and 2. They take Ag as a reference element, for which they have determined the E.A. with an absolute SI method which consists of a measurement of the temperature dependence of the ratio (thermionic electron current  $i_e$ )/(negative ion current  $i_-$ ) on impact of an Ag atom beam upon a tungsten wire of controllable temperature. In this way they obtained  $E.A.(Ag) = (1.90 \pm 0.15)$  eV. Their relative measurements covered the atoms Sb, Bi, In, Cu, Sn, Pb, Si, and Ge.<sup>13,14,23</sup>

All of these methods assume thermal equilibrium on the metal surface. It may be that this condition is not fulfilled when beams of atoms (or complex vapor) impinge on a heated metal surface and interact with the atoms of the surface for an average time which is difficult to estimate. Moreover, if a complex vapor is used<sup>12,14,23</sup> for one of the "atomic" beams, one has to assume complete dissociation on the hot surface unless one measures the ratio of negative and positive ion current.<sup>13,14</sup> The condition of thermal equilibrium is probably best fulfilled in self-surface-ionization studies, as described by Scheer<sup>24</sup> for W, Ta, Re, and Mo. What one actually measures in SI is an average over many small surface areas of quite different constitution and work function. It has been argued<sup>13</sup> that these local differences cancel out in the summation over the whole surface if the two atom beams impinge on the surface simultaneously. This statement is only true if the two beams interact with exactly the same area of the surface; this condition is not easy to establish experimentally, since two locally separated evaporators have been used<sup>12-14</sup> (and normally have to be used).

It should be mentioned that SI provided good results in the determination of the differences between the

E.A.'s of halogen atoms.<sup>5</sup> It may quite generally be true that SI is capable of giving good numbers for the EA differences between atoms having similar chemical behavior (and in particular similar surface chemistry).

Bakulina and Ionov<sup>12</sup> obtain  $E.A.(Au) - E.A.(Ag) = 1$  eV in a separate experiment, in which they use Ag and Au atomic beams simultaneously. This result, as well as that of Zandberg *et al.*<sup>14</sup> for  $E.A.(Ag) - E.A.(Cu)$ , agrees with our measurements within the quoted<sup>12,14</sup> uncertainties.

Our result for E.A.(Cu) can be compared with theoretical predictions by Clementi<sup>21</sup> (Hartree-Fock calculation including empirical correlation correction) and by Schwarz<sup>22</sup> (pseudopotential calculation). The fact that their electron affinities are, respectively, above and below our measured value by about 0.5 eV indicates the difficulty of calculating accurate E.A.'s for such large atomic systems. Consequently, the method of iso-electronic extrapolation (which empirically accounts for the effects which presently make accurate calculations so difficult) may provide the best estimate for the electron affinities of heavy elements, especially if reliable benchmarks are used. In particular, one can estimate the E.A.'s of the elements in the three long series (K→Cu, Rb→Ag, Cs→Au) via horizontal IE analysis.<sup>16</sup>

In this context we would like to come back to the work of Charkin and Dyatkina<sup>15</sup> and to that by Zollweg.<sup>16</sup> These authors showed that the energy difference between the two configurations  $d^{Ks^2}$  and  $d^{Ks}(K=0, \dots, 10)$  increases nearly linearly with  $K$ . Since it is rather well established<sup>15,16,21</sup> that the ground state configuration of negative ions in the three long periods is  $d^{Ks^2}$ , one can estimate the electron affinities of these atoms, if those for K, Rb, Cs on the one side and those for Cu, Ag, and Au on the other side are known, because thereby the slope of the straight line<sup>25</sup> representing the  $d^{Ks^2} \rightarrow d^{Ks}$  energy differences between the negative ion and the  $d^{Ks}$  neutral atom state is fixed.

Measurements of the E.A.'s of K, Rb, Cs have been reported by Ebinghaus and Neuert<sup>26</sup> (electron impact appearance potential for negative alkali ions from halogen salt vapor) and by Bydin<sup>27</sup> (charge exchange studies). The two sets of data disagree; we prefer here the values given by Weiss<sup>28</sup> (CI calculation);  $E.A.(K) = 0.47$  eV,  $E.A.(Rb) = 0.42$  eV,  $E.A.(Cs) = 0.39$  eV, which should be correct to within about 100 meV.<sup>29</sup>

Using the same procedure as Zollweg<sup>16</sup> we arrive at the values shown in Table II, in which the E.A.'s of the elements of the three long periods (excluding the rare earths) are listed together with the isoelectronic extrapolation values of Charkin and Dyatkina (Glockler's method<sup>30</sup>+correction) and Clementi's<sup>21</sup> numbers. The data of Charkin and Dyatkina<sup>15</sup> were originally adjusted by the authors to provide reasonable numbers for K and Rb. One may readjust their data by normalizing to our Cu and Ag values.

Experimental E.A. determinations are very scarce.

TABLE II. Electron affinities of the elements in the three long series [eV].

	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Clementi <sup>a</sup>	0.92	...	-0.14	0.40	0.94	0.98	-1.07	0.58	0.94	1.28	1.80
Charkin and Dyatkina <sup>b</sup>	[0.50]	-1.62	-0.39	0.15	0.65	0.85	-1.19	0.11	0.72	1.10	1.35
This work (Zollweg <sup>c</sup> method)	[0.47]	-1.62	-0.80	-0.11	0.51	0.85	-1.19	0.14	0.65	1.13	[1.23]
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Charkin and Dyatkina <sup>b</sup>	[0.60]	-0.50	0.30	1.04	1.32	1.28	0.96	1.44	1.34	1.40	1.48
This work (Zollweg <sup>c</sup> method)	[0.42]	-1.74	-0.76	0.08	0.77	0.86	0.63	1.04	1.12	0.40	[1.30]
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
This work (Zollweg <sup>c</sup> method)	[0.39]	-0.54	0.44	-0.78	-0.05	0.98	0.09	1.10	1.58	2.12	[2.31]

<sup>a</sup> See Ref. 21.

<sup>b</sup> See Ref. 15.

<sup>c</sup> See Ref. 16.

Scheer<sup>24</sup> measured E.A.'s for Mo, Ta, W, and Re by self-surface ionization as follows:

$$\text{E.A.}(\text{Mo}) = (1.0 \pm 0.2) \text{ eV},$$

$$\text{E.A.}(\text{Ta}) = (0.8 \pm 0.3) \text{ eV},$$

$$\text{E.A.}(\text{W}) = (0.5 \pm 0.3) \text{ eV},$$

$$\text{E.A.}(\text{Re}) = (0.15 \pm 0.10) \text{ eV}.$$

Except for the case of Ta, there is reasonable agreement between Scheer's data and the extrapolated numbers in Table II.

The number for Pt obtained from this extrapolation (2.12 eV) agrees very well with the photodetachment value<sup>10</sup> ( $2.128 \pm 0.002$ ) eV. This agreement may be fortuitous; though we believe that our IE numbers represent an improvement over those of Zollweg<sup>16</sup> as a result of our using reliable data for Cu, Ag, and Au, we think that they should be viewed rather as a guideline with individual errors of order 100 meV being possible.

In addition to the determination of the electron affinities of Cu and Ag, the present investigation yields numbers for the anisotropy parameter  $\beta$  of the angular distribution of the photodetached electrons. The finding  $\beta = 2.00 \pm 0.03$  for both  $\text{Cu}^-$  and  $\text{Ag}^-$  detachment (at 4880 Å) is in agreement with expectation for removal of an *s* electron in an electric dipole transition under *LS*-coupling conditions.<sup>19b,31</sup>

However, if there is significant spin-orbit interaction a different value for  $\beta$  may result, as has been observed by Niehaus and Ruf<sup>32</sup> in their study of the photoionization of  $\text{Hg}(6s^2\ ^1S_0)$ , where they find  $\beta = 1.68 \pm 0.1$

for formation of  $\text{Hg}^+(6s^2\ ^1S_{1/2})$  at 584 Å. Another example is the photoionization of Cs atoms around 3000 Å. Ejection of the outer 6*s* electron leads into the *p*<sub>1/2</sub> or *p*<sub>3/2</sub> continua, and spin-orbit effects make the radial matrix elements for these two transitions sufficiently different that great deviations of  $\beta$  from 2 will be observed. This result can be predicted from the formulae given by Heinzmann, Kessler, and Lorenz.<sup>33</sup>

Harrison<sup>34</sup> has measured the angular distribution of electrons from photoionization of Zn and Cd atoms (isoelectronic with  $\text{Cu}^-$  and  $\text{Ag}^-$ ). He found  $\beta = 2.02 \pm 0.48$  for  $\text{Zn}^+(^2S_{1/2})$  and  $\beta = 1.97 \pm 0.17$  for  $\text{Cd}^+(^2S_{1/2})$  formation at 1048 Å, which indicates that, as in the case of  $\text{Cu}^-$  and  $\text{Ag}^-$  photodetachment, spin-orbit effects are not important.<sup>35</sup>

It would be interesting to determine  $\beta$  for  $\text{Au}^-$  detachment in order to look for spin-orbit effects. If one compares photodetachment and photoionization of isoelectronic negative ions and atoms respectively (such as  $\text{Au}^-$  and Hg), one may in general expect that the effects of the spin-orbit interaction, which is strongest close to the nucleus, are less pronounced in photodetachment since the extra electron with its rather low binding energy will be located at larger distances *r* from the nucleus than the corresponding electron in the isoelectronic atom.

#### ACKNOWLEDGMENTS

We would like to thank J. L. Hall for a number of stimulating discussions. We appreciate the skillful work by R. Weppner, D. Hendry, and C. Pelander on various

parts of the ion source used in this work. We further acknowledge fruitful discussions with D. Moores and S. T. Manson.

### APPENDIX

The number 1.829 eV for the effective electron affinity of OH arises as follows: the electron affinity of OH has been accurately determined in a recent dye-laser photodetachment experiment<sup>36</sup> and is 1.825<sub>5</sub> eV with an uncertainty of  $\pm 2$  meV. The center of the detached electron peak (at  $h\nu = 2.54$  eV) has been calculated by superimposing the various rotational transitions for some sets of different transition strengths for the various rotational branches and source temperatures between 300°K and 2000°K (assuming Boltzmann equilibrium). The proper term values<sup>37</sup> for OH(<sup>2</sup>Π<sub>1/2</sub>) were used; for OH<sup>-</sup>(<sup>1</sup>Σ<sup>+</sup>), use was made of the experimental result<sup>38</sup> that  $r_e(\text{OH}^-) = r_e(\text{OH})$  to within 0.001 Å in order to determine the rotational constant for OH<sup>-</sup>.

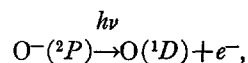
The following rotational transition branches were taken into account:

$$\begin{array}{lll} P3: \text{OH}^-(^1\Sigma; J^-), & \text{OH}(^2\Pi_{3/2}; J^- - 1/2), & J^- \geq 2; \\ Q3: \text{OH}^-(^1\Sigma; J^-), & \text{OH}(^2\Pi_{3/2}; J^- + 1/2), & J^- \geq 1; \\ R3: \text{OH}^-(^1\Sigma; J^-), & \text{OH}(^2\Pi_{3/2}; J^- + 3/2), & J^- \geq 0; \\ P1: \text{OH}^-(^1\Sigma; J^-), & \text{OH}(^2\Pi_{1/2}; J^- - 3/2), & J^- \geq 2; \\ Q1: \text{OH}^-(^1\Sigma; J^-), & \text{OH}(^2\Pi_{1/2}; J^- - 1/2), & J^- \geq 1; \\ R1: \text{OH}^-(^1\Sigma; J^-), & \text{OH}(^2\Pi_{1/2}; J^- + 1/2), & J^- \geq 0. \end{array}$$

In the following discussion the notation  $S(P3)$  refers, e.g., to the strength of the  $P$  branch transition terminating on OH(<sup>2</sup>Π<sub>3/2</sub>), and  $S(P1)$  refers to transitions terminating on <sup>2</sup>Π<sub>1/2</sub>. If the transition strengths of the  $P$  and  $R$  branches are taken to be the same, i.e.,  $S(P3) = S(R3)$ ,  $S(P1) = S(R1)$ , with the possibility  $S(P3) \neq S(P1)$ ,  $S(R3) \neq S(R1)$ , and if  $S(Q3)$ ,  $S(Q1)$  are varied relative to  $S(P3, R3)$  and  $S(P1, R1)$  and relative to each other, the results of these calculations are almost independent of the assumed ion source temperature (to within 1 meV); they yield an average detachment energy ( $3.5 \pm 1.5$ ) meV higher than E.A.(OH), i.e., ( $1.829 \pm 0.004$ ) eV.

If one allows for the possibility  $S(P3) \neq S(R3)$ ,  $S(P1) \neq S(R1)$ , the results are more sensitive to the assumed ion source temperature  $T$  and the calculated center varies more, as one would expect. For the temperature range  $300^\circ\text{K} < T < 2000^\circ\text{K}$  and the following combinations of relative transition strengths  $S(P3, P1, Q3, Q1, R3, R1) = (1, 1, 4, 2, 2, 2), (2, 2, 4, 2, 1, 1), (2, 2, 2, 2, 1, 1), (1, 1, 2, 2, 2, 2), (1, 1, 1, 1, 2, 2)$ , and  $(2, 2, 1, 1, 1, 1)$  it was found that the center of the detachment peak will be positioned within a  $\pm 8$  meV range around a value, which corresponds to an effective E.A.(OH) of 1.829 eV.

The number 1.465 eV for the average O<sup>-</sup> detachment energy emerges as follows: the electron affinity of O is taken to be 1.462 eV; this value is based on some recent tunable laser photodetachment experiments,<sup>39</sup> carried out on the onset for O(<sup>1</sup>D) production:



with the result that

$$\text{E.A.}(\text{O}) = \left( \begin{array}{c} +0.003 \\ 1.462 \\ -0.007 \end{array} \right) \text{eV}.$$

The fine-structure splitting between the <sup>2</sup>P<sub>3/2</sub>–<sup>2</sup>P<sub>1/2</sub> levels in O<sup>-</sup> is obtained from an isoelectronic extrapolation procedure<sup>9</sup> (which was tested and found very good for the cases of S<sup>-</sup> and Se<sup>-</sup>) as 22.5 meV with an uncertainty believed to be no more than 1 meV. We use these values for E.A.(O) and the O<sup>-</sup> spin-orbit splitting in preference to earlier work.<sup>40</sup> Averaging over the six possible fine-structure transitions O<sup>-</sup>(<sup>2</sup>P) → O(<sup>3</sup>P) by using either the statistical model<sup>8</sup> or the prediction by Rau and Fano<sup>41</sup> for the transition strengths leads to the value

$$\left( \begin{array}{c} +0.005 \\ 1.465 \\ -0.009 \end{array} \right) \text{eV}$$

for the “effective electron affinity” of O, which corresponds to the center of the O<sup>-</sup> detached electron peak.<sup>42</sup> The uncertainty introduced by the lack of knowledge of the relative population of the O<sup>-</sup>(<sup>2</sup>P) levels in combination with the uncertainty for the O<sup>-</sup> spin-orbit splitting is no more than  $\pm 2$  meV.

\* Work supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by U.S. Army Research Office-Durham, under Contract No. DAHCO4 72 C 0047.

† On leave from Fakultät für Physik, Universität Freiburg; support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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