Laser photodetachment measurement of the electron affinity of atomic oxygen

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The electron affinity of atomic oxygen, an important calibration standard in negative-ion photoelectron spectroscopy, has been determined by tunable-laser photodetachment in a coaxial laser–ion-beam spectrometer to be 11 784.645 ± 0.006 cm^{-1}. In addition, the spin-orbit splitting between the $^2P_{3/2}$ and $^2P_{1/2}$ states of O^- was found to be 177.13 ± 0.05 cm^{-1}.

We have determined the electron affinity of atomic oxygen by threshold photodetachment of O^- in a coaxial laser–ion-beam spectrometer, resulting in an improved accuracy of approximately three orders of magnitude. Since O^- is generally used as a calibration standard in negative-ion photoelectron-spectroscopy experiments,[1-3] most electron affinities determined by this technique depend on the accepted value of the electron affinity of oxygen. This quantity has been measured previously by photodetachment of O^- with broad-band (≥ 100 Å) light sources,[4] radiative capture of electrons by O atoms,[5] and photoionization measurements of the threshold for ion-pair formation from O_2.[6] The currently accepted value of 1.462 ± 0.003 eV has been derived from a comparison of these and other experimental results.[1] Several atomic electron affinities have been determined to considerably better than 1 meV accuracy by threshold photodetachment with a tunable dye laser,[3,7-12] but O^- has not been studied previously with this technique as the infrared (ir) dyes needed to probe the threshold region were unavailable. The combination of a cw infrared dye laser with the greatly reduced Doppler widths obtained in a coaxial ion-beam spectrometer[13] permits the determination of the electron affinity $E_{EA}(O)$ to μeV accuracy. [Note that $E_{EA}(O)$ here is equivalent to the previously used notation EA(O).] We have used this approach to obtain an accurate value for $E_{EA}(O)$, as well as an improved value for the $^2P_{3/2}-{}^2P_{1/2}$ splitting in O^-.

The coaxial ion-beam spectrometer used in this work has been described in detail elsewhere.[14] The negative-ion beam and laser interacted collinearly over 30 cm, and both the neutrals and electrons resulting from photodetachment were detected. The 10-nA O^- beam was generated from N_2O in a hot-discharge source and was injected into the interaction region at 3.2 keV. The dye laser could be configured[15] as a standing-wave cavity for broad-band scans and as a ring cavity for single-mode scans. In the standing-wave configuration, the laser linewidth was approximately 0.5 cm^{-1} with a birefringent tuner (BRT) as the sole tuning element. The addition of a thin etalon narrowed the linewidth to 0.05 cm^{-1}. In the ring configuration, the laser was tuned by rotating a Brewster plate. An intracavity Mach-Zehnder interferometer[16] was locked to the cavity mode to prevent mode hopping while scanning. The ring-laser frequency drifted by about 1 MHz/sec unless it was stabilized by an external reference cavity. However, based on other photodetachment studies in which narrow autodetachment resonances were observed, the residual Doppler width in the ion beam is known to be 10–30 MHz, depending on the ion-source conditions.[14,17-19] With this intrinsic resolution, locking the ring laser to an external cavity was considered unnecessary. The dye used was LDS 821 (Exciton) pumped with all lines of an Ar^+ laser. With 7 W of pump power, typical outputs were 500 mW with the BRT only and 100 mW in single mode. The ir-laser wavelength was measured with a wave meter which included a polarization-stabilized single-mode He-Ne reference laser.[20] This laser was in turn calibrated by heterodyning it with another single-mode He-Ne laser which could be locked to a series of accurately known I_2 transitions.[21] Since the wave meter measured the ratio of the ir and He-Ne wavelengths in air, it was necessary to account for the different refractive index of air at the two wavelengths and the local atmospheric pressure in converting the ir wavelength to vacuum wave numbers.[22]

Figure 1 shows the O^- photoelectron signal as a function of laser frequency with the laser operating in the broad-band mode using only the BRT. Six thresholds can be seen, resulting from the fine-structure transitions $O^-(^2P_{3/2,1/2}) \rightarrow O(^3P_{2,1,0}) + e^-$. The ordering of the fine-structure levels is shown in Fig. 1. The neutral fine-structure splittings have been measured to extremely high precision ($< 10^{-4}$ cm^{-1}) in laser magnetic-resonance experiments,[23,24] and the O^- splitting was previously found[25] to be 177.4 ± 1.6 cm^{-1} by photoelectron spectroscopy. All six transitions primarily involve s-wave detachment, and the photodetachment cross section near each threshold should follow the Wigner law,[26]

$$\sigma \propto (E - E_{th})^{1/2} \quad . \tag{1}$$

The $^2P_{3/2} \rightarrow 3P_2$ threshold energy corresponds to the electron affinity since these are the ground states for O^- and O, respectively. Figure 1 was constructed from five 100-cm^{-1} frequency scans. Since the laser frequency was measured only at the endpoints of each scan, the uncertainty in the frequency axis in Fig. 1 can be as high as several cm^{-1}, due to the nonlinearity of the BRT. In order to determine the electron affinity and O^- spin-orbit splitting more accurately, considerably shorter scans were taken at higher resolution near the appropriate thresholds.

The result of a single-mode scan near the electron-affinity threshold is shown in Fig. 2. The interval between the points was 0.001 cm^{-1}, and the signal acquisition time was 10 sec/point. Wave-meter readings were taken at the beginning and end of the scan, which was assumed to be linear in frequency. Although tuning the laser by Brewster-plate rotation resulted in a slightly nonlinear dependence of the laser frequency on the angle of rotation, the maximum deviation from linearity was less than 0.001 cm^{-1} for the scan

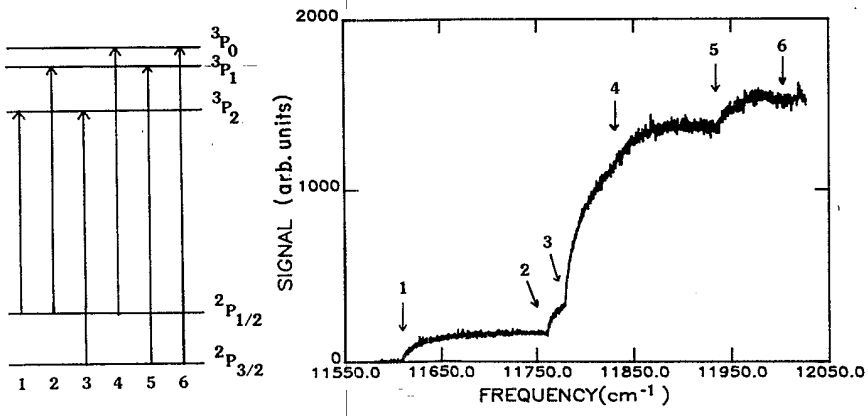

FIG. 1. Low-resolution photodetachment spectrum of O^-. The numbered thresholds are from the transitions $O^-(^2P_{3/2,1/2}) \rightarrow O(^3P_{2,1,0}) + e^-$. The O^- and O fine-structure levels are shown at left.

shown in Fig. 2 and was therefore ignored. The data in Fig. 2 were taken with the laser propagation direction antiparallel to the ion beam; a second scan was taken with the laser direction reversed to account for the Doppler shift. This procedure made it unnecessary to know the ion-beam velocity to high accuracy.

The data in Fig. 2 were fit to Eq. (1) using a nonlinear least-squares program. This yielded $E_{\rm th}^a = 11\,776.925 \pm 0.006$ cm^{-1} for the photodetachment threshold. The result of the scan in which the laser was parallel to the ion beam was $E_{\rm th}^p = 11\,792.376 \pm 0.006$ cm^{-1}. These error bars include the 95%-confidence limits as determined by the fitting program and the uncertainty in the reproducibility of the wave-meter readings; each contributed ± 0.003 cm^{-1}. The electron affinity is obtained from the two thresholds by

$$E_{\rm EA}(\mathrm{O}) = \tfrac{1}{2}(E_{\rm th}^a + E_{\rm th}^p)\left[1 - \left(\frac{v}{c}\right)^2\right]^{1/2} , \qquad (2)$$

where the relativistic term comes from the second-order Doppler shift, which is 0.003 cm^{-1} for a beam energy of 3.2 keV. The result is

$$E_{\rm EA}(\mathrm{O}) = 11\,784.645 \pm 0.006 \text{ cm}^{-1}$$
$$= 1.461\,122 \pm 0.000\,003 \text{ eV} .$$

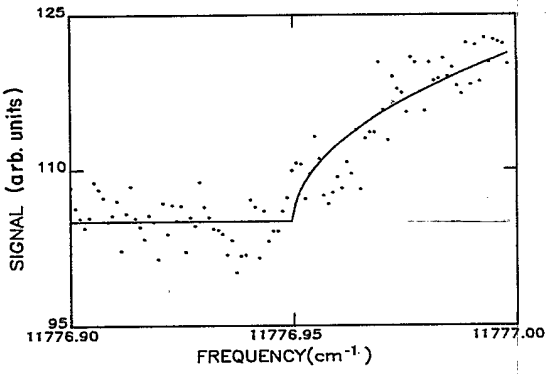

FIG. 2. High-resolution scan of the $^2P_{3/2} \rightarrow {}^3P_2$ (electron-affinity) threshold. Solid line shows computer-generated fit to Eq. (1).

Note that nearly all the uncertainty in $E_{\rm EA}(\mathrm{O})$ when expressed in eV is from the 2.6-ppm uncertainty in the conversion between cm^{-1} and eV.[27]

To determine the spin-orbit splitting between the $^2P_{3/2}$ and $^2P_{1/2}$ states of O^-, the regions near the $^2P_{1/2} \rightarrow {}^3P_2$ and $^2P_{1/2} \rightarrow {}^3P_1$ thresholds in Fig. 1 were scanned using a thin etalon in the standing-wave cavity ($\Delta\bar{\nu} = 0.05$ cm^{-1}). These thresholds were less distinct than the electron-affinity threshold. This was expected, since the $O^-(^2P_{1/2})$ population in the ion beam should be somewhat less than $O^-(^2P_{3/2})$. In addition, the $O^-(^2P_{1/2})$ photodetachment cross sections near threshold are predicted to be smaller than the $O^-(^2P_{3/2})$ cross section near the electron-affinity threshold.[28] The two $O^-(^2P_{1/2})$ thresholds were measured with the laser antiparallel to the ion-beam and corrected only for the first-order Doppler shift. The results were

$$E_{\rm th}(^2P_{1/2} \rightarrow {}^3P_2) = 11\,607.53 \pm 0.05 \text{ cm}^{-1} ,$$
$$E_{\rm th}(^2P_{1/2} \rightarrow {}^3P_1) = 11\,765.81 \pm 0.05 \text{ cm}^{-1} .$$

The spin-orbit splitting, $E_{\rm SO}$, can be obtained from

$$E_{\rm SO} = E_{\rm EA}(\mathrm{O}) - E_{\rm th}(^2P_{1/2} \rightarrow {}^3P_2) \qquad (3)$$

or

$$E_{\rm SO} = E_{\rm EA}(\mathrm{O}) + E_{\rm SO}(^3P_1, {}^3P_2) - E_{\rm th}(^2P_{1/2} \rightarrow {}^3P_1) , \qquad (4)$$

where $E_{\rm SO}(^3P_1, {}^3P_2)$, the splitting between the oxygen $^3P_1$ and $^3P_2$ states, is known from laser magnetic-resonance studies to be 158.303 cm^{-1}.[23] The results from (3) and (4) are 177.12 cm^{-1} and 177.14 cm^{-1}, respectively. Our final value from averaging these two is 177.13 ± 0.05 cm^{-1}. This can be compared to the photoelectron-spectroscopy value (177.4 ± 1.6 cm^{-1}, Ref. 25) and an earlier value of 181 ± 4 cm^{-1} obtained by isoelectronic extrapolation.[8] We therefore observe that, for both the electron affinity and O^- spin-orbit splitting, our more precise measurements are well within the error bars of the previous best values.

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