

Photoelectron spectroscopy of IO^-

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Photoelectron spectroscopy has been used to obtain the $\text{IO}(^2\Pi_{3/2}, ^2\Pi_{1/2}; v') + e^- \leftarrow \text{IO}^- (^1\Sigma^+; v'')$ spectrum. In addition to providing an accurate adiabatic electron affinity, this measurement gives direct structural information on the anion and reports the first observation of the ground state $^2\Pi_{3/2}-^2\Pi_{1/2}$ spin-orbit splitting. The chemistry of IO is of particular interest, in part because of its similarity to ClO, which plays a well-known, major role in ozone depletion in the stratosphere,¹ and due to its own role as a tropospheric ozone sink.²

IO is known to possess a $^2\Pi_{3/2}$ ground state.³ Both the ground state of IO and its excited ($A\ ^2\Pi_{3/2}$) state have been well characterized spectroscopically.⁴⁻⁶ Because of its possible role in catalytic destruction of ozone, there have been a number of measurements of reactions of the ground state radical with atmospheric oxidants NO_2 , HO_2 , and IO .⁷⁻⁹ The spin-orbit splitting of the neutral has been estimated to be $\approx 2330\text{ cm}^{-1}$, but has never been observed.¹⁰ Because the anion ($X\ ^1\Sigma^+$) is formed by addition of a weakly antibonding (π^*) electron to the IO ground state electronic configuration, it is expected to have a longer equilibrium bond length and a lower vibrational frequency than the neutral ground state. All estimate of the electron affinity of IO have come from threshold energies of endothermic ion-molecular reactions. Reactions of I^- with

O_2 , CO , CO_2 or SO_2 to form IO^- have placed the electron affinity of IO between 2.1 and 2.6 eV.¹¹⁻¹⁴

The negative ion photoelectron spectrometer used in this experiment is described in detail elsewhere.^{15,16} IO^- is made in a flowing afterglow source. The reactant O^- ion is produced in a microwave discharge with trace amounts of O_2 seeded in the helium buffer gas. A subsequent fast reaction of O^- with CF_3I produces the IO^- .¹⁷ Ions are gently extracted, focused, accelerated, mass selected with a Wien filter, and decelerated to 40 eV before entering the laser interaction region. The single frequency (351.1 nm) output of an argon ion laser is coupled into a high finesse build up cavity and the kinetic energy of the photodetached electrons is determined using a hemispherical electrostatic energy analyzer with 9 meV resolution. The absolute electron energy scale is calibrated by photodetachment of O^- , which has a well known electron affinity.¹⁸

The 351.1 nm photoelectron spectrum of IO^- taken at the "magic angle"¹⁹ is displayed in Fig. 1. Photoelectron intensity is plotted vs electron kinetic energy. The upper scale is electron binding energy, which is given by the difference between the photon energy and the measured electron kinetic energy. We observe two vibrational progressions separated by $2091(40)\text{ cm}^{-1}$, corresponding to the

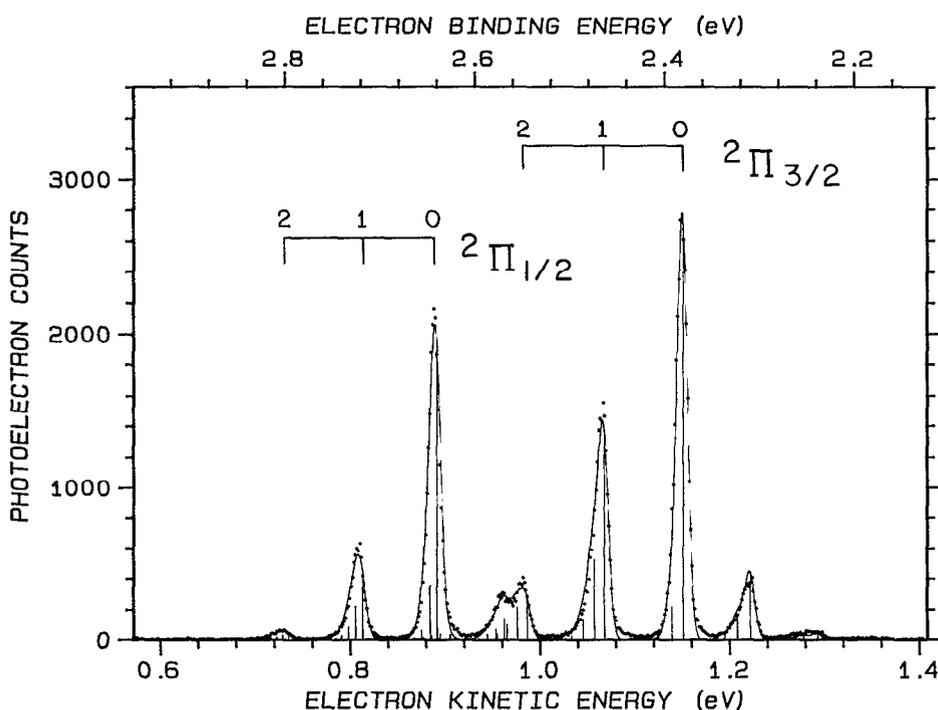


FIG. 1. The ultraviolet photoelectron spectrum of IO^- taken with 351.1 nm photon energy. Two progressions, $\text{IO}(^2\Pi_{3/2}, ^2\Pi_{1/2}; v' = 0, 1, 2) + e^- \leftarrow \text{IO}^- (^1\Sigma^+; v'' = 0)$ are designated in the photoelectron spectrum.

TABLE I. Spectroscopic constants for both spin-orbit states of neutral IO and IO⁻. Unless otherwise indicated, all values were determined from this work.

State	r_e , Å	ω_e , cm ⁻¹	$\omega_e X_e$, cm ⁻¹	Energy, cm ⁻¹
IO $X^2\Pi_{1/2}$	1.887(10)	658(25)	4.37 ^a	2091(40)
IO $X^2\Pi_{3/2}$	1.8677 ^b	681.6 ^b	4.37 ^b	0
IO ⁻ , $X^1\Sigma^+$	1.929(10)	581(25)	4.37 ^a	-19180(40) ^c

^aNot determined, but constrained to this value in the Franck-Condon analysis.

^bConstrained to these experimental values from Ref. 4 for the Franck-Condon analysis.

^cCorresponds to EA(IO) = 2.378 ± 0.005 eV.

spin-orbit components of the IO ground state. Hot bands due to the $^2\Pi_i(v' = 0) \leftarrow ^1\Sigma^+(v'' = 1)$ transitions are observed for each spin orbit state to the right of the vibrational origin designated (0). The adiabatic electron affinity of IO [2.378(5) eV] was determined from the binding energy of the vibrational origin transition. A rotational correction was obtained by simulating a rotational contour, with a rotational temperature of 400 K, convolved with a Gaussian function.²⁰

Unknown molecular constants for IO⁻ and IO were determined from Franck-Condon simulations of the spectrum for each of the electronic transitions observed. All of the electronic states were treated as Morse oscillators, and the Franck-Condon factors were calculated by numerically integrating the overlap between the Laguerre wave functions of the neutral and anion species. By fitting directly to the data, both the energy and intensity information provided by the photoelectron spectrum are simultaneously used to determine the unknown molecular constants. For the simulation of the IO($^2\Pi_{3/2}$) - IO⁻($^1\Sigma^+$) transition, molecular parameters for the $X^2\Pi_{3/2}$ state were fixed to literature values⁴ and the anion bond length (r_e), vibrational frequency (ω_e), and vibrational temperature were allowed to vary in a least-squares fit to the data. For the Franck-Condon simulation of the IO($^2\Pi_{1/2}$) - IO⁻($^1\Sigma^+$) transition, the anion parameters were fixed to the values found in the previous simulation and the neutral parameters were optimized. Since we are unable to accurately determine the anion and neutral $^2\Pi_{1/2}$ vibrational anharmonicities, these were fixed at the measured $^2\Pi_{3/2}$ value. The vibrational temperature of the anion was determined to be 730(150) K. The fitting procedure determines only the absolute value of the bond length change upon photodetachment. The anion bond length was assumed to be longer than both neutral bond lengths, be-

cause the photodetached electron originates from an antibonding orbital. The smaller vibrational frequency observed for the anion is consistent with this expectation. The results of the Franck-Condon analyses with the neutral $^2\Pi_{3/2}$ parameters are summarized in Table I. The uncertainties shown represent changes in the parameters which significantly degraded the quality of the fit to the data.

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