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Autodetaching States in I^-†

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Collisional excitation of negative iodine ions produces a group of peaks between 5 and 8 eV in the detached-electron spectrum. The autodetaching states decaying into these peaks appear to have dominant configurations of the form (I^+ core)$6s6l$. No structure is apparent at lower electron energies.

In a recent Letter,[1] Mandl and Hyman reported the observation of a resonancelike structure in the photodetachment cross section of I^- centered about 2.5 eV above the energy of the neutral iodine ground state. The work we report, in which the I^- autodetaching states are populated by collision processes, locates the lowest doubly excited I^- states at somewhat higher energies. A new assignment for the photodetachment structure is required, most likely in terms of a d-wave shape resonance built on the $5p^5$ neutral ground state.

If the state giving the structure in photodetachment is excited in a heavy-particle collision, we would expect to observe a peak in the electron distribution at the state energy. We find, however, that the electron spectrum from 0.5 to 5 eV seems to contain only the smoothly varying contribution from direct detachment, rising with decreasing electron energy. If the 2.5-eV feature has a width at half-maximum of less than 0.5 eV, we estimate that it is produced under the conditions of our experiments with a cross section less than 3×10^{-19} cm^2.

On the basis of the good agreement of the present results with the expected pattern and location for the doubly excited states, Mandl and Hyman now suggest[2] that the photodetachment structure comes from absorption to a d-wave shape resonance. That interpretation also provides better agreement with the observed width. The very short lifetime implied by that width (less than the collision time at our energies) makes observation

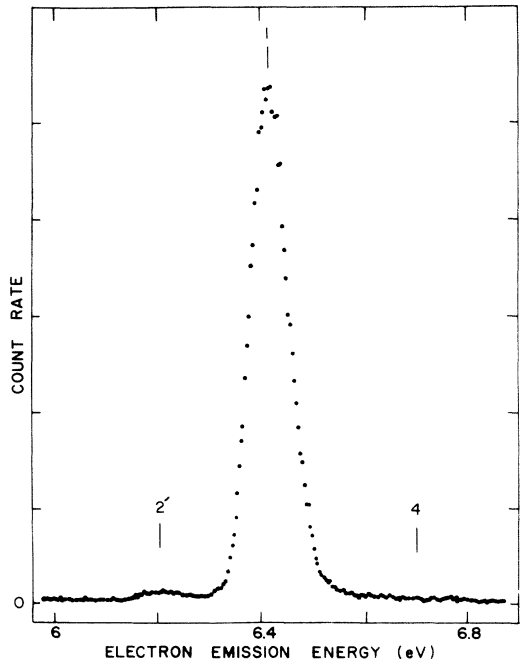

FIG. 1. Major feature in the electron spectrum from collisions of I^- on He. Beam energy 2 keV, observation angle 20°.

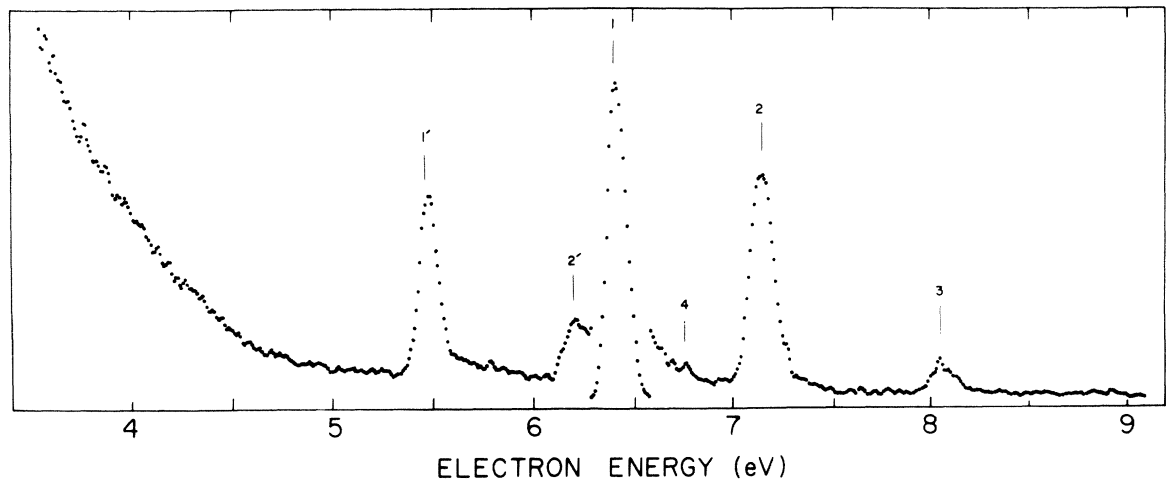

FIG. 2. Electron spectrum for I^- on He at 2 keV beam energy and 30° observation angle. Electron energies have been transformed to the frame of the moving ion. The major peak is suppressed by a factor of 10. A three-point binomial smoothing has been used to reduce the scatter.

of such a feature in a heavy-particle collision unlikely.

The measurements on I^- were made using the apparatus and procedures previously described in reports on similar states of O^-, Cl^-, and F^-.[3-5] A beam of I^- ions is extracted from a duoplasmatron ion source[6] running with hydrogen as the support gas, to which KI is added by evaporation from a second filament. The beam, at energies of 1–3 keV, is magnetically momentum analyzed and focused into a differentially pumped chamber containing the helium target gas. Electrons ejected from the region of the I^--on-He collisions pass into a parallel-plate electrostatic energy analyzer and are detected with a channel electron multiplier. The resulting spectra show a background of electrons detached directly into continuum states, with superimposed peaks due to electrons from the decay of excited autodetaching states.

The major feature in the collisional detachment spectrum of I^- on He (originally observed by Bydin[7]) is shown in Fig. 1. An absolute electron energy scale was established by comparing the location of this peak to the 10.11-eV peak in the spectrum of O^- on He.[3,8] The I^-- and O^--beam currents were adjusted to give equal beam space-charge densities so that energy shifts due to beam potentials would cancel out. The correctness of this procedure was checked at one beam energy by obtaining the peak locations as a function of beam charge density and extrapolating to zero beam density. Any possible drifts in contact potentials were minimized by switching

TABLE I. Autodetaching states of I^-: tentative identification.

Feature	Decay energy[a] (eV)	Tentative I^- configuration	I^0 final state
1	6.41	$5p^4(^3P_2)6s^2$	$5p^5(^2P_{3/2})$
1′	5.47		$5p^5(^2P_{1/2})$
2	7.15	$5p^4(^3P_1$ or $^3P_0)6s^2$	$5p^5(^2P_{3/2})$
2′	6.21		$5p^5(^2P_{1/2})$
3	8.06	$5p^4(^1D_2)6s^2$	$5p^5(^2P_{3/2})$
4	6.75	$5p^4(^3P_2)6s6p$	$5p^5(^2P_{3/2})$

[a]This equals the energy of the I^- state relative to $I^0(^2P_{3/2})$ for the unprimed features. Uncertainties are ±0.06 eV absolute, ±0.02 eV relative.

back and forth between the two beams at short intervals. The usual[9] vector addition relates the peak energy at a given observation angle and beam energy to the electron emission energy in the frame of the moving beam particle. A series of runs at different angles and beam energies gave results consistent to within ±0.02 eV, and accurate to ±0.06 eV on an absolute basis.

A number of weaker peaks appear at nearby energies, as illustrated by the spectrum in Fig. 2. Spacings between the peaks reflect the interval in the neutral iodine ground term[10] (the final state of the autodetaching decay) and the spacing between terms in the grandparent I^+ ground configuration.[11] Our provisional assignments of the dominant configurations in these I^- autodetaching states appear in Table I.

The lowest doubly excited configuration $5p^4(^3P_2)$-$6s^2$ is by far the most strongly excited state for I^--on-He collisions. This contrasts with the case for the light halogens F^- and Cl^-, where L-S coupling and selection rules apply, and the corresponding triplet term is not observed.[4,5] Widths of all the I^- features could not be distinguished from purely instrumental widths.

By placing a gas cell in the beam ahead of the collision region, it was possible to strip the extra electron from a large fraction of the beam particles. Diverting the charged beam fraction then gave a fast neutral I beam. The electron spectrum from neutral I on He showed only weak structure, and nothing which would interfere with any of the assigned I^- peaks.

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Dependence of Transition Moment on Internuclear Separation in Na_2†

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The electronic transition moment between the $B\,^1\Pi_u$ and $X\,^1\Sigma_g$ states of the Na_2 dimer is measured as a function of internuclear separation by monitoring the laser-induced atomic fluorescence signal.

Historically the Condon approximation[1]—the neglect of the dependence of electronic transition moments on internuclear separation—has provided spectroscopists with a useful tool for unraveling molecular spectra. Modern molecular-structure calculations, however, assert that this approximation is of rather limited validity. Clearly a direct measurement of the transition moment's spatial variation would be valuable in that it would provide a sensitive check on the accuracy of *ab initio* wave functions. Experimental efforts to measure this function have been limited mainly to the r-centroid technique[2]; this has proven to be useful only in particular molecules and over a limited range of internuclear separations. In this Letter we employ the technique of laser-induced atomic fluorescence to obtain directly the electronic transition moment between the $B\,^1\Pi_u$ and $X\,^1\Sigma_g{}^+$ states of diatomic sodium as a function of internuclear separation, for separations between 2.7 and 3.7 Å.

The theory of induced atomic fluorescence has been discussed in the literature recently.[3] It was argued that transient resonances between a laser