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Effect of Resonances on the Near-Threshold Electron Detachment Cross Sections of F^-†

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Very narrow (~2 meV) ^1D and ^1P shape resonances above the ground state of atomic fluorine lead to electron and photon near-threshold F^- detachment cross sections of approximately $(2-3)\times 10^{-15}$ and 4×10^{-14} cm^2, respectively, and could affect the F-atom production rates in the relativistic-electron-beam H_2/F_2 lasers.

I report the first use of the multiconfiguration close-coupling (MCC) formalism[1] in the problem of low-energy-electron impact detachment of negative atomic ions. During calculations of low-energy-electron impact ionization of the negative atomic fluorine ion, I found a very narrow ($\Gamma \sim 0.002$ eV) ^1D shape resonance in the elastic cross section at 0.009 eV above the F ground state. This resonance causes high near-threshold values of the electron and photon detachment cross sections of F^-.

There have been several studies of electron impact ionization of negative atomic ions[2] but, with two exceptions,[2a,2g] only H^- was treated; and, even for this case, no unique prescription for the near-threshold detachment process has yet evolved. References 2a and 2g contain, to my knowledge, the most exhaustive theoretical treatments of the electron detachment problem for other atoms (Na^-, Cl^-, Hg^-, and O^-) to this date. Finite attachment (detachment) cross sections to outer s or p orbitals were discussed by Massey and Smith[2a] and the detachment cross section of weakly bound p electrons in O^- was, indeed, found to be large close to threshold by Wanatabe and Miida.[2g] The Bethe-Born approximation has been shown to compare reasonably with the experimental detachment cross section in O^- for energies of 20–50 eV, but not well at lower energies, and to lead to predictions at variance with experimental data for H at higher energies.[2h]

The present study was stimulated by estimates of energy deposition in atmospheric-pressure, relativistic-electron-beam–pumped H_2/F_2 mixtures,[3] according to which the initial free-fluorine production rate could be dominated, on nanosecond time scales, by the resonant dissociative process $e + F_2 \rightarrow F_2^- \rightarrow F + F^-$ (if the F_2^- state had a width of 2 eV) and that F^- formation could also contribute if the electron detachment cross section were as large as 7×10^{-15} cm^2. Detachment cross sections of such magnitude in F^- are perhaps doubtful because they imply an overestimation of available experimental data for H^- and O^- by factors of 10 and 70, respectively.[3b] I shall discuss the e-F_2^- system at a later date, and here present results for e-F^-.

In the Born approximation, the detachment cross section $\sigma^d(E)$, is given by[2a]

$$\sigma^d(E) = \frac{m^2}{2\pi\hbar^4}\int_0^{k_{\max}}\iint d\Omega\, d\Omega'\kappa^2 |M_{\kappa,k}|^2 d\kappa, \tag{1a}$$

with

$$M_{\kappa,k} = \frac{4\pi}{K^2}\int \psi_0 \psi_\kappa e^{iK\vec{n}\cdot\vec{r}} d\tau, \qquad \psi_\kappa = \sum F_s(r) P_s(\cos\theta) i^s (2s+1), \tag{1b}$$

so that

$$\int |M_{\kappa,k}|^2 d\Omega' = \frac{32\pi^4}{3K}\{[\int_0^\infty F_0 P_{2p}(r) J_{3/2}(Kr) r^{3/2} dr]^2 + 2[\int_0^\infty F_2 P_{2p}(r) J_{3/2}(Kr) r^{3/2} dr]^2 + [\int_0^\infty F_1 P_{2p}(r) J_{1/2}(Kr) r^{3/2} dr]^2\} + \dots, \tag{1c}$$

where P_{2p} is the orbital of the bound $2p$ electron and the other quantities are as in Ref. 2a.

The close-coupling approximation can be applied to this problem just as for electron impact ionization of neutral atomic hydrogen,[4] and photo-

TABLE I. Angular momentum values of electrons scattered by gound and excited terms of F.

Configuration	$1s^22s^22p^5$	$1s^22s^22p^4(^3P)3s$		$1s^22s^22p^4(^3P)3p$						$1s^22s^22p^4(^1D)3s$
$LS\Pi$ ↓ \ Terms →	$^2P^o$	$^4P^e$	$^2P^e$	$^4P^o$	$^4D^o$	$^2D^o$	$^2S^o$	$^4S^o$	$^2P^o$	$^2D^e$
$^1S^e$	1	...	...	...	...	...	...	...	1	...
$^3S^e$	1	...	...	1	...	...	...	...	1	...
$^3S^o$	...	1	1	...	2	2	0	0	...	...
$^1P^e$	1	...	0,2	...	...	1,3	1	...	1	2
$^1P^o$	0,2	...	1	...	...	2	...	...	2	1,3
$^3P^e$	1	0,2	0,2	1	1,3	1,3	1	1	1	2
$^3P^o$	0,2	1	1	0,2	2	2	...	...	0,2	1,3
$^1D^e$	1,3	...	2	...	...	1,3	...	...	1,3	0,2,4
$^1D^o$	2	...	1,3	...	...	0,2,4	2	...	2	1,3
$^3D^e$	1,3	2	2	1,3	1,3	1,3	...	...	1,3	0,2,4
$^3D^o$	2	1,3	1,3	2	0,2,4	0,2,4	2	2	2	1,3

ionization of neutral atoms[5] or the alkali negative ions.[6] The cross section for the process

$$e + F^-(2p^6\,{}^1S) \to F(2p^5\,{}^2P^o) + e' + e'', \qquad (2)$$

is evaluated by approximating part of the final state with MCC solutions $[F_0(r)$ and $F_2(r)]$ for elastic and, in a multistate expansion, inelastic scattering, $e + F \to F$ (or F^*) $+e$ (e').

With the usual assumptions of total L, S, Π conservation,[1] the allowed values of the *scattered* electron angular momentum (l_2) (see Table I) imply that the dominant near-threshold contributions can be expected, in this formalism, from the $^{1,3}P^o$, $^{1,3}D^o$, and $^{1,3}S^e$ partial waves. For an initial estimate, I neglect higher-order terms[2a] and disregard the triplet states because of Eq. (4) below, so that only the $^1P^o$ and $^1D^o$ MCC contributions are needed. This should give a lower limit on the detachment cross section.

Alternatively, using the modified Bethe-Born approximation, previously applied to H^- with an approximation for electron impact ionization,[2e,7] we get

$$\sigma^d(E) = \frac{1}{\pi\alpha E}\int_0^{(E-I)/2} \frac{\sigma^{\mathrm{ph}}(E')}{I+E'} \ln\frac{4E\tau}{I+E'}\, dE'. \qquad (3)$$

Here $\sigma^{\mathrm{ph}}(E')$ is the photoionization cross section; E' the ejected photoelectron energy; I the ionization potential (for my case, the electron affinity of $F^- = 3.5$ eV) and $\tau \simeq 1$. The limit of $\frac{1}{2}(E-I)$ instead of $(E-I)$ in the integral of Eq. (3) allows for electron exchange.[2d,2e]

To use Eq. (3), only one ($^1P^o$) partial wave is needed, according to

$$h\nu + F^-(2p^6\,{}^1S) \to {}^1P^o \to F(2p^5\,{}^2P^o) + \begin{Bmatrix} \epsilon s \\ \epsilon d \end{Bmatrix}. \qquad (4)$$

As noted above, sample $^1D^o$ (and other) calculations were, however, carried out for use with Eq. (1) and also to determine the size of the other possible contributions (cf. Table I) given that such contributions cannot be *a priori* eliminated because the electron detachment process equation (2) is not restricted by the optical selection rules, as is that of Eq. (4).

The $^1D^o$ resonance was discovered after a discontinuity in the elastic cross section was investigated, using established techniques,[8] with increasingly finer energy grids. Over the range of $(6.0-7.0)\times10^{-4}$ Ry, the $^1D^o$ phase shift increases by π and a Breit-Wigner fit yields $\Gamma = 0.002$ eV and $E_\Gamma = 0.009$ eV.[9]

Although the $^1D^o$ contribution to the elastic section is small (except over the resonance region where it rises to approximately $2000\pi a_0^2$) and, by selection rules, this partial wave cannot contribute directly to the photoionization cross section, the resonance can have a dramatic effect on both the photon and electron detachment cross sections, as I now discuss.

From Table I and Eqs. (1) and (3) we see that if the d-exciting electron is indeed resonant, structures can be expected in both the individual (ϵd) and total ($\epsilon s + \epsilon d$) contributions to photoabsorption and, via either Eq. (1) or directly from Eq. (3), in the electron detachment cross sections. Resonant d-wave peaks have been previously pointed out in photodetachment cross sections of Cl^- at about 12 eV,[2a,10] and a Ramsauer-type minimum was also predicted in the s-wave e-Cl elastic cross section in the range 0.1–1.0 eV.[10] Such a "d-wave interference peak"[10] at nearer-threshold energies in F^- could be qualitatively understood by the tighter binding of the $2p$ in comparison with the $3p$ electrons, making the initial "capture" of the incident low-energy electrons more likely and the resultant "shape" resonances narrower. To examine further this possibility, *the* $^1P^\circ$ *calculations* were repeated over a finer mesh of 1×10^{-5} to 2×10^{-3} Ry and the total and individual *scattered electron* partial wave (l_2) contributions to the detachment cross sections [cf. Eq. (1)] are shown in Fig. 1.

At energies very close to the threshold, and also well beyond the resonance position, s-wave scattering dominates as it should because this is, *in toto*, a low-energy region. As the resonance is approached from below, the d-wave contribution begins to increase and, over the energy range of 6×10^{-4} to 1.4×10^{-3} Ry, completely determines the total $^1P^\circ$ partial wave cross section. This is shown in Fig. 1 with filled circles for the cross sections at energies where this total is indistinguishable from the d-channel contribution. As can be seen in the figure, the $^1P^\circ$ resonance position is around 1.2×10^{-3} Ry but because in this case the $l_2 = 0$, 2 channels are coupled, the width is smaller (as could be expected) and certainly less than 1×10^{-5} Ry—the finest grid used over this energy region. Thus, the use of close-coupled final-state functions in Eq. (1), instead of single-channel solutions only, shows that the resonance in the $l_2 = 2$ channel is also evident when the (degenerate $l_2 = 0$, 2) channels are coupled. In addition to a large near-threshold elastic cross section, the resonance causes the near-threshold enhancement of both the electrodetachment and photodetachment cross sections of F^-.

The positions and widths of the resonances may be modified by initial-state distortion and spin-

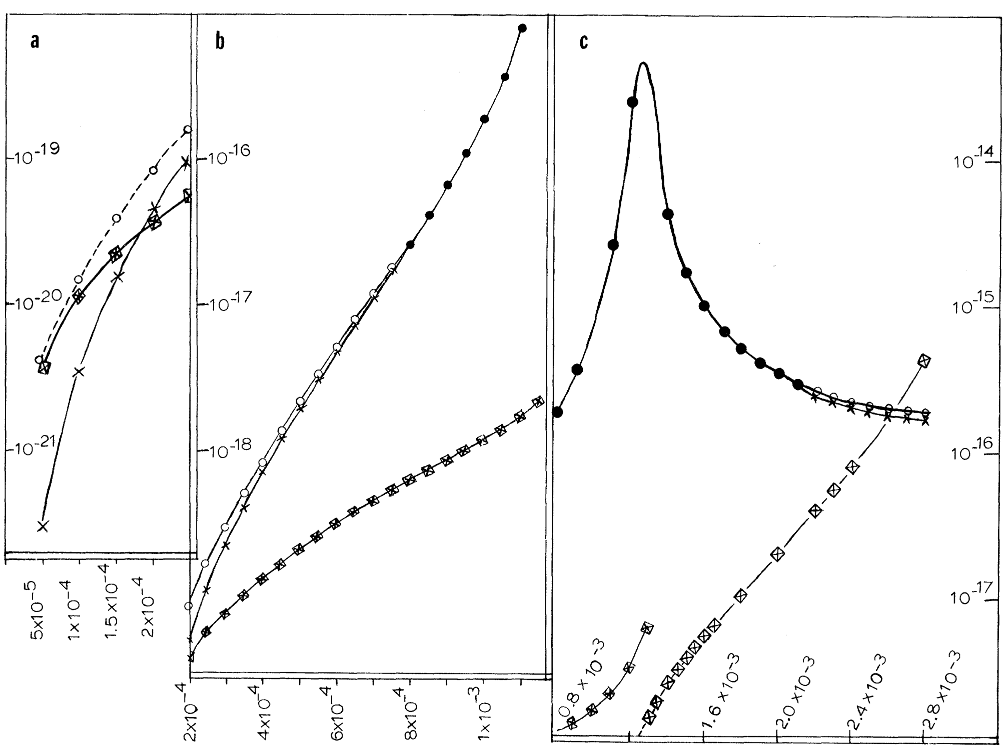

FIG. 1. e-F^- detachment over the resonance region. Partial-wave (total $LS\Pi = {}^1P^\circ$) close-coupling contributions to electron detachment cross section of F^- over the resonance region. Note the different energy scales. ⊠, s; ×, d; ○, total; ●, d and total indistinguishable (see text).

orbit coupling that have not been allowed for in our model.[11] The exact position of the $^1D^\circ$ resonance is of interest because the low-lying (50 meV) $^2P^\circ$ $J=\frac{1}{2}$ term, connected to the lower ground-state ($J=\frac{3}{2}$) term by the magnetic-dipole forbidden transition, can be reached by electron excitation only. If the resonance position is higher than the one obtained here, additional population of the upper $^2P^\circ$ state by resonance decays would be yet another instance of excitation of a metastable term via a negative ion.[12]

My results support the hypothesis that negative ions could enhance the free-fluorine production rate.[3b] Note also that in lasers with upper states pumped primarily by decays of negative ions, the experimental requirement for monoenergetic —in the sense of electron beam width narrower than resonance width—electron beam distribution[12] can now be relaxed, because with picosecond pulses the copious production of secondary electrons in relativistic-electron-beam H_2/F_2 mixtures ensures high densities of F^- formation. The role of the resonances could be tested experimentally with frequency-doubled 49.43-μm (H_2O^{18}) or 50.5-μm (D_2O) laser lines.

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