

Autoionization and interchannel mixing in atomic fluorine: The $2p^4(^1S)ns,md$ Rydberg series

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Experimental data on the spectroscopic and dynamic properties of the $2p^4(^1S)ns,md$ series between the 1D and 1S thresholds of atomic fluorine are presented. These series are observed through their decay into the allowed $2p^4(^3P)\epsilon l$ and $2p^4(^1D)\epsilon l$ ionization channels. The $(^1S)ns\ ^2S$ resonances are broad windows, and the $(^1S)md\ ^2D$ resonances are narrow peaks in the principal $2p^4(^1D)\epsilon l$ channel. The $2s2p^6\ ^2S$ resonance is located at 20.99(1) eV and is seen to interact strongly with the nearby $2p^4(^1S)4s\ ^2S$ resonance. The resulting structure can serve as a sensitive marker for this interchannel mixing. Except for the interacting resonances, the data are found to be in satisfactory accord with eigenchannel R -matrix results for the total cross section.

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Recently, we employed synchrotron-radiation-based electron spectrometry for a detailed investigation of the autoionization resonances in atomic fluorine between the $F^+ 2p^4\ ^3P$ and 1D ionization thresholds [1]. We have now used the same technique to determine the spectroscopic parameters of the $2p^4(^1S)ns,md$ Rydberg series, and, more importantly, to delineate the dynamic characteristics of these autoionizing series as they manifest themselves in the *partial* cross sections. At the same time, we have located the $2s2p^6\ ^2S$ resonance, which is of special interest because of its interaction with the members of the $(^1S)ns\ ^2S$ series. To our knowledge, up to now, none of these various series has been observed experimentally, and the only available information comes from an eigenchannel R -matrix calculation of the *total* cross section [2].

The experiment was carried out at the Synchrotron Radiation Center in Wisconsin using our electron spectrometer system equipped with a microwave-driven discharge tube for the production of F atoms. The apparatus and procedures were the same as have been described in our previous work on fluorine [1]. The 4-m normal incidence monochromator used was set to a bandpass of 21 pm for the bulk of the measurements, and the $(^1S)ns,md$ series between the 1D and the 1S thresholds at 20.011 and 22.9919 eV were recorded by observing the emitted electrons at the pseudomagic angle in the constant ionic state (CIS) mode of electron spectrometry. This procedure is equivalent to the measurement of the relative partial cross sections for the final ionic states, $F^+ 2p^4(^3P)$ and $F^+ 2p^4(^1D)$, which are populated in the decay of the autoionizing resonances.

We calibrated the energy scale of the monochromator by using the energies of the Xe resonance lines Nos. 1, 4, and 9 as given by Codling and Madden [3] and the Ar $3s \rightarrow np$, $n=4-6$, lines measured by Madden *et al.* [4]. The energies of these lines lie between 20.7 and 21.4 eV and between 26.6 and 28.5 eV, respectively, and are accurate to better than 8×10^{-5} . For conversion we used the factor 1239.842 nm eV.

The $F 2p^4(^1S)ns\ ^2S,md\ ^2D$ series are shown in Fig. 1 as they manifest themselves in the $2p^4(^1D)$ continuum channel. The $md\ ^2D$ series appears as very sharp narrow lines, while the $ns\ ^2S$ series appears as rather broad windows in

close proximity to the $m=n-1$ members of the $md\ ^2D$ series. The energies and quantum defects for the series members up to 10 are listed in Table I. These values are derived from the spectrum of Fig. 1 and two additional spectra recorded with a finer mesh at a bandpass of 21 and 7 pm for the higher members of the series. Since the line profiles have a very high value for the shape parameter q , as for the md series, or a value close to zero, as for the ns series, the maxima or minima of the respective profiles are taken as the resonance energies. The quoted uncertainties in the energies include the calibration error of ± 4 meV, which was somewhat larger than it was in the previous work [1]. The values of the quantum defect δ given in Table I are based on the reduced Rydberg constant $Ry = 13.6054$ eV and the 1S_0 series limit of 22.9919 eV [5-7]. We notice a decrease in the quantum defect δ with increasing quantum number. A slight dependence is expected to occur [8]; however, series interactions such as $2p^4(^1D_2)md\ ^2D \leftrightarrow 2p^4(^1S_0)md\ ^2D$ might also contribute. On the other hand, a reduction of the line energies by about 3 meV, which would be compatible with

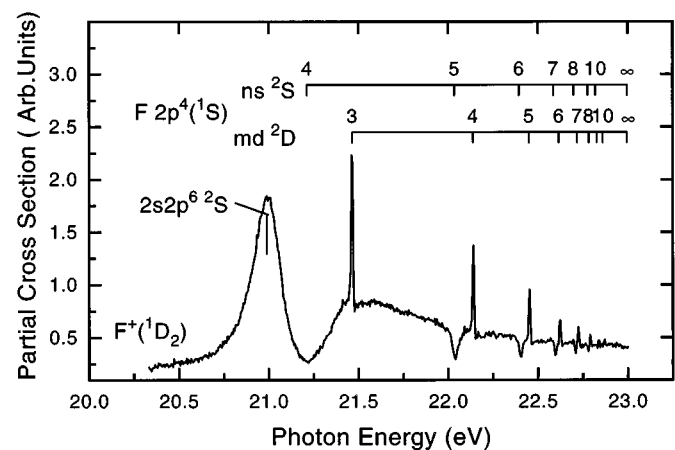


FIG. 1. Autoionizing resonances of atomic fluorine measured in a CIS scan on the $F^+ (^1D)$ ionic state in the range between the 1D and 1S thresholds. The spectrum is recorded with a bandpass of 21 pm at the pseudomagic angle and is fully corrected. Small peaks visible 50 meV below the $3d$ and $4d$ members are due to the $^2P_{1/2}$ excited state of fluorine.

TABLE I. Energies and quantum defects δ for the members of the two autoionizing series converging to the 1S limit of atomic fluorine at 22.9919 eV.

| Members n, m | Energy (eV) | | δ | |
|-------------------|-------------|-----------|-----------|-----------|
| | $ns\ ^2S$ | $md\ ^2D$ | $ns\ ^2S$ | $md\ ^2D$ |
| 3, | 18.218(5) | | 1.312(5) | |
| 4,3 | 21.213(6) | 21.467(5) | 1.234(4) | 0.013(4) |
| 5,4 | 22.035(5) | 22.139(5) | 1.229(9) | 0.007(11) |
| 6,5 | 22.397(5) | 22.449(5) | 1.22(2) | -0.01(2) |
| 7,6 | 22.587(5) | 22.617(5) | 1.20(3) | -0.02(4) |
| 8,7 | 22.700(5) | 22.718(5) | 1.17(5) | -0.05(6) |
| 9,8 | 22.776(6) | 22.784(6) | 1.06(8) | -0.09(9) |
| 10,9 | 22.820(7) | 22.829(7) | 1.11(8) | -0.2(1) |

the calibration uncertainty and earlier results [1], would lead to a lesser dependence of δ on n^* .

The energy of the peak observed earlier at 18.214(2) eV [1,9], and generally believed to correspond to the $(^1S)3s\ ^2S$ excitation, was determined to be 18.218(5) eV. Its quantum defect of 1.31 is somewhat greater than the values found for the subsequent members of the 2S series. This value is within the range the quantum defect may assume for the first member of a series, but it cannot be regarded as an entirely unambiguous confirmation of the assignment. The quantum defects for the $(^1S)ns$ and $(^1S)md$ series members are close to the values of 1.26 and 0.008 for the corresponding $(^1D)ns$ and $(^1D)md$ series members [1], and compa-

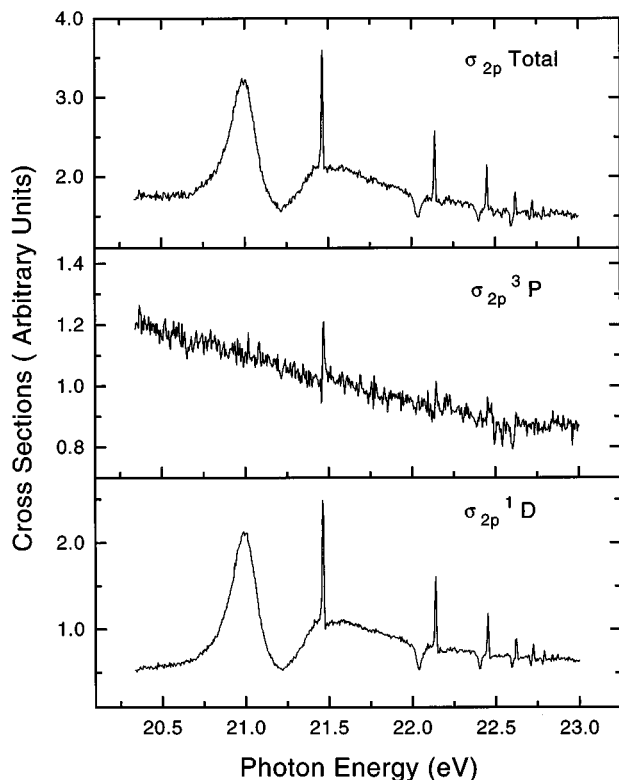


FIG. 2. Partial and total cross sections in the region between the 1D and 1S thresholds of atomic fluorine. Ordinate scales are normalized to one another at 21.8 eV.

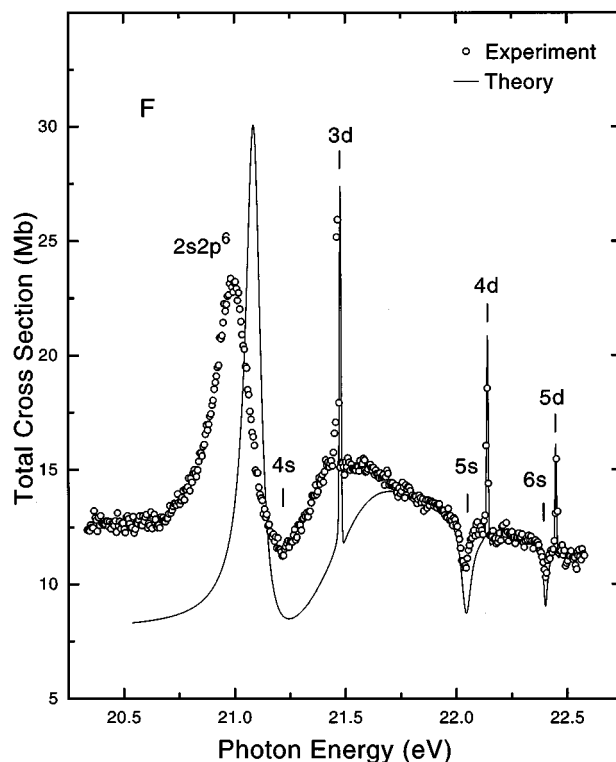


FIG. 3. Comparison of the theoretical (Ref. [14]) and experimental total cross sections. The experiment is normalized to the theoretical cross section at 21.8 eV.

table with the Hartree-Slater values of 1.20 and 0.003 calculated for s and d electrons [10].

At 20.99(1) eV a strong and broad peak, about 0.15 eV wide, is observed in the $^1D\epsilon l$ channel. We assign it to the $F\ 2s2p^6\ ^6S$ excited state arising from the $2s \rightarrow 2p$ transition. To our knowledge, this excitation has not been observed before, and various predictions of its energy, width, and shape have varied widely. The position of the peak as observed by us differs from that of 21.055 eV evaluated by Kelly [11], 21.13 eV predicted by Cowan *et al.* [12], 22.14 eV calculated by Aspromallis and Nicolaides [13], and 21.08 eV calculated by Robicheaux [14]. We note that the latter value, obtained in an eigenchannel R -matrix model, is higher than the energy of 20.58 eV calculated earlier [2]. In either case, the accuracy is believed [14] to be only about ± 0.3 eV for this particular state. The differences in the predicted energies are not surprising, because the position is strongly influenced by the interaction with the $ns\ ^2S$ series members, particularly the $4s$ member. As a consequence, the $2s2p^6\ ^6S$ resonance is not an isolated resonance with well defined properties as expressed, for example, by the Fano parameters. We may, however, speak of *apparent* energies, widths, and shapes for ease of discussion. It is surprising that the interaction does not introduce a noticeable effect on the quantum defect of the 2S series, especially the lower members $n=4$ and $n=5$ (cf. Table I).

The dynamic information contained in the partial cross sections, $\sigma_{2p}(LS)$, is shown in Fig. 2 by way of CIS spectra for the two accessible ionic states $F^+ (^1D)$ and $F^+ (^3P)$. The spectra are fully corrected for background and photon flux, and they are normalized to each other at $h\nu=21.8$ eV

with the aid of a photoelectron spectroscopy spectrum, which yielded $\sigma_{2p}(^3P)/\sigma_{2p}(^1D)=1.0(1)$.

The relative total cross section is also shown in Fig. 2 as the sum of the partial cross sections. While the average $\sigma_{2p}(LS)$ are of similar magnitude in both channels, except just above the 1D threshold, where $\sigma_{2p}(^3P)$ dominates, the resonance features are much more pronounced in $\sigma_{2p}(^1D)$ than in $\sigma_{2p}(^3P)$. For example, the md 2D resonances are stronger in 1D by about a factor of 3 than in 3P , where interference with the direct photoionization channel leads to a dispersive profile of these resonances. Not unexpectedly, the ns 2S resonances are not seen in 3P ; they are forbidden in LS coupling to autoionize into 3P . This applies also to the $3s$ 2S resonance, whose suspected appearance below the 1D threshold depends solely on spin-orbit coupling for non-radiative decay [1,9,15]. By contrast, the ns 2S resonances exhibit two major points: (i) They can interact with the nearby strong $2s2p^6$ 2S resonance; and (ii) they readily decay into the $^1D\epsilon l$ continuum. The first point is of greatest import, because it leads to the window-type resonances in F observed in this experiment and first predicted by Robicheaux and Greene [2], and it makes these windows unusually wide. This is particularly evident in the $4s$ 2S window, which is also devoid of the Fano shape pertaining to isolated resonances. In turn, the $2s2p^6$ 2S resonance is also distorted. The observed apparent width is about double the calculated width [14], as seen in Fig. 3. The tail on the low-energy side occurs in both the experiment and theory. Since the eigenchannel R -matrix calculation [14] places the $2s2p^6$ 2S state close to the $4s$ 2S state, the latter appears to be pushed toward higher energy and spread out. By contrast, the observation gives the $4s$ 2S state more the resemblance of a window-type resonance. If the two states are spaced further apart yet, as indicated in an earlier R -matrix calculation [2], the $2s2p^6$ 2S resonance is considerably broadened and the $4s$ 2S resonance is close to an isolated window resonance due to the reduced interaction.

Figure 3 gives an overall comparison between our data and the length-gauge theoretical results [14] based on the model given by Robicheaux and Greene [2,16]. The theoretical calculations of the cross sections in the length gauge and in the velocity gauge differ by 10%. The theoretical results are convoluted with the experimental bandpass of 21 pm, and the experimental total cross section is matched at $h\nu=21.8$ eV to the theoretical value of 13.8 Mb. There is good agreement between the data measured and the theoretical results, except for the region near the interfering $2s2p^6$ 2S and $4s$ 2S resonances. The positions of both the sharp md 2D , $m\geq 4$, resonances and the window-type ns 2S , $n\geq 5$, resonances are in very good agreement. The windows are more pronounced in the theoretical total cross section than in the experimental one, which may indicate a variance in the partitioning of σ_{2p} into the $\sigma_{2p}(^3P)$ and $\sigma_{2p}(^1D)$ components.

In summary, the $(^1S)ns,md$ autoionizing series, as well as the $2s2p^6$ 2S resonance have been investigated. Both spectroscopic and dynamic properties have been determined and compared with theory. The apparent energy, width, and profile of the $2s2p^6$ 2S resonance are seen to provide a sensitive measure for the correct assessment of the interactions with the $(^1S)ns$ 2S members. More detailed data, which include the widths of the lower members of the autoionizing series and the photoelectron angular distribution parameters, will be presented in the near future.

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