Electron attachment in F_2: Conclusive demonstration of nonresonant, s-wave coupling in the limit of zero electron energy

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Dissociative electron attachment to F_2 has been observed in the energy range $0 \leq \varepsilon \leq 140$ meV, at a resolution of 6 meV (full width at half maximum). Results show conclusively a sharp, resolution-limited threshold behavior consistent with an s-wave cross section varying as $\varepsilon^{-1/2}$. Two accurate theoretical calculations predict only p-wave behavior varying as $\varepsilon^{1/2}$. Several nonadiabatic coupling effects leading to s-wave behavior are outlined.

There has existed for the past six years a significant discrepancy between experimental and theoretical cross sections for dissociative attachment in molecular fluorine at electron energies below 100 meV. Beam measurements of Chantry[1] for the process $e+F_2 \rightarrow F+F^-$ show an increasing cross section with decreasing ε. Recent swarm-unfolded cross sections of McCorkle *et al.*[2] are in qualitative agreement with Chantry, and are increasing down to a lower energy limit of 30—40 meV.

Theoretical, *ab initio* calculations of dissociative attachment in fluorine have been carried out by Hazi, Orel, and Rescigno[3] in terms of intersecting F_2 ($^1\Sigma_g^+$) and F_2^-($^2\Sigma_u^+$) potential energy curves. These calculations treat only the resonant, $^2\Sigma_u^+$ contribution to the dissociative attachment, so that the cross section satisfies the $\varepsilon^{1/2}$ threshold law for this channel; i.e., the cross section vanishes at zero electron energy. Calculations by Bardsley and Wadehra[4] similarly were unable to account for the experimental indication of an increase in cross section. While they obtained good agreement with Chantry's data down to 150 meV, their cross sections continued to decrease due to the $l=1$, p-wave behavior inherent to their calculation.

The present experimental study was undertaken to characterize the attachment process at extremely low electron energies, especially the region below 40 meV. It was felt that experimental limitations and uncertainties of the previous data[1,2] could not lead to any firm conclusion regarding s- or p-wave threshold behavior. The experimental uncertainties, including that of the present measurements, can be summarized as follows.

Chantry:[1] 80-meV [full width at half maximum (FWHM)] electron energy resolution and a 100-meV uncertainty in the energy scale. The cross sections below 100 meV could be in error by as much as a factor of 2, and the deconvoluted results below about 40 meV are unreliable. However, the energy-integrated cross section from zero to 0.1 eV is reliable.

McCorkle *et al.*:[2] $\sim$ 50-meV resolution and $\sim$20-meV uncertainty in the energy scale. The swarm-rate unfolded cross sections below 40 meV are unreliable due to uncertainties in calculation of the swarm electron energy distribution function at each reduced electric field (see an analogous discussion in Ref. 5). Cross sections above 40 meV have a statistical uncertainty of about 25%.

Present results: 6-meV resolution and 1.8-meV uncertainty in the energy scale. Cross sections throughout the range 0—140 meV have total statistical uncertainty of 25%, including uncertainty in the thermal electron attachment rate constant of McCorkle *et al.*[2]

The technique used in the present measurements was the Kr photoionization method described in previous publications.[6,7] Significant modifications in the present work dealt only with the handling of fluorine. Because of the corrosive nature of F_2, the collision chamber was rid of all materials (plastics, greased seals, and a sodium salicylate window) which could react with the fluorine. Standard precautions were taken in the gas-handling system.[8] These included use of a stainless-steel barricade, a Monel automatic pressure regulator with remote valve handles, and a hydrogen fluoride trap. All gas lines were of stainless steel, with steel or Teflon gaskets. The fluorine itself was supplied[9] as a mixture of 8% F_2 in 92% Kr, with stated purities of 98% (F_2) and 99.995% (Kr).

The collision cell, quadrupole mass analyzer, and gas lines were baked for 24 h at 120°C to remove any adsorbed water. Fluorine was then admitted, and the apparatus "passivated" over a period of several days. The passivation procedure was monitored by measuring the F^- signal rate, which increased by a factor of about 3 during this time. When no further significant increase was noted (less than 5% over four hours) accumulation of the final data via multichannel scaling was initiated. A total of four spectra were acquired over a period of two weeks: two at 12-meV (FWHM) resolution, each requiring 3-h accumulation time; and one each at 8.5- and 6.0-meV resolution requiring 8—10-h accumulation time apiece. Total pressure in the collision chamber 0.27 Pa, with approximately 8% due to F_2.

We point out that no damage to the differentially pumped, osmium-coated diffraction grating was detected, but the channel electron multiplier at the output of the mass analyzer (see Fig. 1 of Ref. 7) had to be replaced after a total of four days' exposure.

Attachment line shapes for the process $e+F_2 \rightarrow F+F^-$ are shown in Fig. 1 at three electron-energy resolutions. One clearly sees that, as the resolution is increased from 12 to 6.0 meV (FWHM), the threshold peak "sharpens up" to a width given by the instrumental resolution, a re-

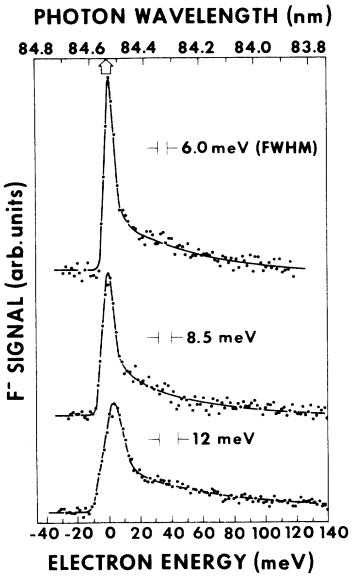

FIG. 1. Electron-attachment line shapes for the process $e+F_2 \rightarrow F+F^-$ at the three indicated electron-energy resolutions. Solid lines are computed fits to the experimental data. Arrow on top scale indicates the threshold for ionization to the $Kr^+(^2P_{1/2})$ level at 84.542 nm.

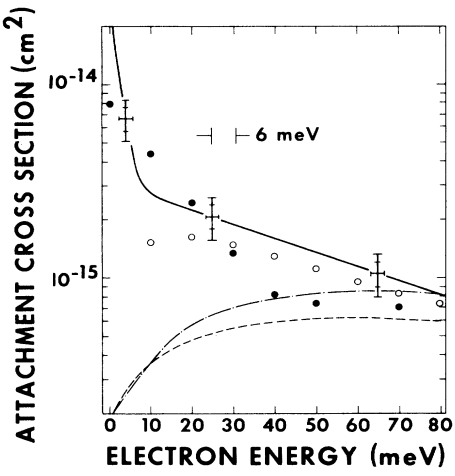

FIG. 2. Dissociative attachment cross sections in F_2 in the energy range 0—80 meV. Results are ●, beam measurements (Ref. 1). ○, swarm-unfolded data (Ref. 2); ——, present threshold photoionization results; —·—·—·, *ab initio* theoretical results of Hazi *et al.* (Ref. 3); — — —, semiempirical theoretical results of Bardsley and Wadehra (Ref. 4).

sult consistent with presence of an infinite cross section at threshold. Further increases in resolution were not feasible due to loss of signal, compounded by the fact that F_2 had the smallest attachment cross section measured, to date, in our laboratory. However, threshold features of 4.0 meV width have been noted in other *s*-wave attaching molecules.[9]

As in studies with other molecules,[5,7] the attachment line shapes were unfolded from the spectrometer slit function in terms of an attachment cross section of the form

$$\sigma_A(\varepsilon)=N[a\varepsilon^{-1/2}\exp(-\varepsilon^2/\lambda^2)+\exp(-\varepsilon/\gamma)]\ , \quad (1)$$

where the parameters a and λ are determined from the unfolding procedure, and γ from the high-energy ($\varepsilon > 10$ meV) portion of the line shape. The factor N is determined by normalization to the thermal-attachment rate constant $k(\bar{\varepsilon})$ at 298 K for F_2, taken as[2] $(1.8\pm0.36)\times10^{-8}$ cm^3/s. Details of this normalization procedure can be found in Ref. 7. The parameters a and λ were obtained by unfolding a total of four spectra, and γ from the four spectra and from an additional measurement at 12 meV resolution and longer channel dwell times. Results of the computed fit to the data are shown as the solid lines in Fig. 1. The final parameter values in Eq. (1) are $a=0.153$ eV$^{1/2}$, $\lambda=4.72\times10^{-3}$ eV, $\gamma=6.04\times10^{-2}$ eV, and $N=3.15\times10^{-15}$ cm^2. Attachment cross sections are shown in Fig. 2, with comparisons to both other experiments and theory. Error bars in the present data are given as double sided, with the smaller error (12% at the 1σ level) representing systematic uncertainties in the shape of the cross section, and the larger representing errors in shape added in quadrature with errors in $k(\bar{\varepsilon})$ (20% at the 1σ level[2]). We point out that the energy-integrated cross section of the present results is 2.1×10^{-16} cm^{2}eV, in good agreement with Chantry's range of[1] $(1.4\text{—}3.2)\times10^{-16}$ cm^{2}eV.

For laser-plasma modeling purposes, we show in Fig. 3 electron-attachment rate constants obtained by integrating Eq. (1) with a Maxwellian electron energy distribution function at mean energy $\bar{\varepsilon}$. One sees excellent agreement among three experiments, whereas the flowing afterglow results of Sides, Tiernan, and Hanrahan[10] appear to be low. The difference between present data and theories is again a reflection of the *s*-wave versus *p*-wave difference.

Results of Figs. 1, 2, and 3 illustrate clearly the contribution of an incoming, *s*-wave electron to dissociative attachment to F_2. This capture process corresponds to $^2\Sigma_g^+$ symmetry for the e-F_2 compound system, since the elec-

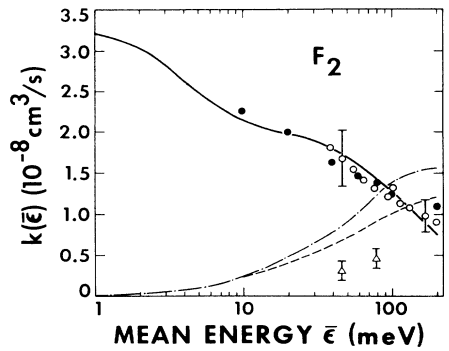

FIG. 3. Electron-attachment rate constants as a function of mean energy $\bar{\varepsilon}$. Present data are integrated with a Maxwellian electron-energy distribution function. Symbols are the same as in Fig. 2, and triangles (△) are additional data of Sides, Tiernan, and Hanrahan (Ref. 10).

tronic ground state of F_2 is $^1\Sigma_g^+$. So far, there is no satisfactory theoretical interpretation of the observed "zero-energy" peak in terms of $^2\Sigma_g^+$ scattering or negative ion resonance states. In what follows, we offer a few qualitative comments to stimulate additional theoretical work.

The dissociation limit $F^-(^1S)+F(^2P)$ gives rise to four molecular electronic states: the well-known[3,4] $^2\Sigma_g^+$ ground state of F_2^-, and three mostly repulsive states $^2\Pi_g$, $^2\Pi_u$, and $^2\Sigma_g^+$. Although no calculations have yet been reported for these excited states of F_2^- (as far as we know), results available for the isoelectronic molecular ion Ne_2^+ suggest[11] that the $^2\Sigma_g^+$ resonance state will have the highest energy at the equilibrium internuclear distance of $F_2(X\,^1\Sigma_g^+)$. Potential energy curves for the relevant states of F_2 and F_2^- based on calculations,[3,4] and estimates from state splittings in[11] Ne_2^+, are shown in Fig. 4. If one assumes that, at the equilibrium internuclear distance of F_2, the vertical excitation energy corresponding to $^2\Sigma_u^+$-$^2\Sigma_g^+$ is the same as that calculated[11] for Ne_2^+ (~ 3.5 eV), then the repulsive potential energy curve of $F_2^-(^2\Sigma_g^+)$ is estimated to cross that of $F_2(^1\Sigma_g^+)$ at $R\sim 1.8$ Å, and at an energy which is already 1.0 eV above the $v=0$ ground state of F_2. As a result, it is unlikely that direct capture of the incoming, s-wave electron into the $^2\Sigma_g^+$ resonance of F_2^- is responsible for the large dissociative attachment cross section at threshold. Instead, it is probably due to some nonadiabatic coupling associated with the breakdown of the Born-Oppenheimer separation of electronic and nuclear motions. We note that 1.0-meV electron spends about 5×10^{-14} s within a 10-Å diameter region surrounding F_2. This time is comparable to the vibrational period (4×10^{-14} s) of F_2. One type of nonadiabatic coupling is electron-rotation (Coriolis) interaction[12] between the $^2\Sigma_g^+$ state associated with the incoming electron and the $^2\Pi_g$ resonance of F_2^-. The potential energy curve of the corresponding state in Ne_2^+ is calculated to be slightly attractive,[11] so that the $^2\Pi_g$ state should be the lowest excited state of F_2^- also. Another possibility is nonadiabatic interaction between the initial $^2\Sigma_g^+$ state and the well-known $^2\Sigma_u^+$ resonance, due to terms which arise when the molecular Hamiltonian is expressed in terms of electronic coordinates relative to the separated nuclei.[13] In any case, it is clear that additional theoretical work, including *ab initio* calculations of the higher resonance states of F_2^-, will be necessary to explain the observed threshold peak in the dissociative attachment cross section of F_2.

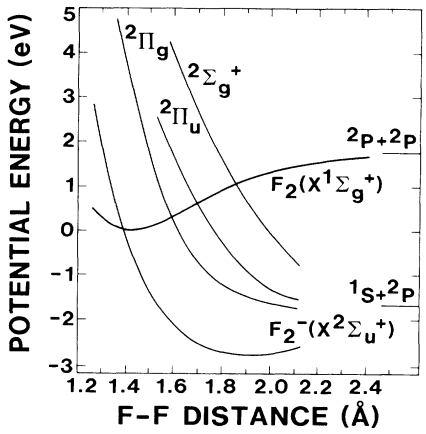

FIG. 4. Potential curves for states of F_2 and F_2^-. The states $^1\Sigma_g^+(F_2)$ and $^2\Sigma_u^+(F_2^-)$ are from Refs. 3 and 4. The states $^2\Sigma_g^+(F_2^-)$, $^2\Pi_u(F_2^-)$, and $^2\Pi_g(F_2^-)$ are estimated from Ne-Ne^+ state splittings of Ref. 11.

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