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Observation of p-Wave Threshold Behavior in Electron Attachment to F_2 Molecules

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Using the high resolution laser photoelectron attachment method, we demonstrate that the cross section for F^- formation due to electron capture by $F_2(X\,^1\Sigma_g{}^+)$ molecules at very low energies exhibits p-wave threshold behavior. This finding confirms the theoretical expectation that low-energy attachment to F_2 proceeds through the $F_2{}^-(^2\Sigma_u{}^+)$ p-wave shape resonance in contrast with previous experimental claims for s-wave threshold behavior.

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Molecular fluorine F_2 is an important constituent in electrically excited gas lasers [1]. Correspondingly, much interest has existed for a long time in low-energy collisions of electrons with F_2, resulting in vibrational excitation (VE), neutral dissociation and ionization, or in dissociative electron attachment (DEA) forming $F^- + F$. Unfortunately, F_2 is an aggressive gas which is rather difficult to work with, and until now experimental data for the mentioned processes are rather scarce. To our knowledge, only one measurement has been carried out on VE [2]. The DEA process has been investigated by several groups, using electron swarms (see [3], and references therein), electron beams [4–6], and a vacuum ultraviolet (VUV) photoelectron attachment method [7,8]. In the electron beam work, carried out with energy widths around 0.1 eV [5,6], a peak was observed in the F^- yield at near-zero energies, more or less compatible with swarm-unfolded cross sections [8]. In a TPSA (threshold photoelectron spectroscopy for attachment) experiment, Chutjian and Alajajian [7] found a narrow spike very close to zero energy with a width compatible with the optical resolution of 6–12 meV. They interpreted their findings as a "conclusive demonstration of non-resonant, s-wave coupling in the limit of zero electron energy" (for s-wave capture the cross section at very low electron energies E behaves as $\sigma(E) \propto E^{-1/2}$ [9]).

From the theoretical side, however, electron attachment to $F_2(X\,^1\Sigma_g{}^+)$ molecules at very low energies is expected to proceed by p-wave ($l = 1$) electron capture because of the *ungerade* parity of the lowest anion resonance state $F_2{}^-(^2\Sigma_u{}^+)$ [10–19]:

$$e^-(E; l = 1) + F_2(X\,^1\Sigma_g{}^+) \rightarrow F_2{}^-(^2\Sigma_u{}^+) \rightarrow F^- + F. \tag{1}$$

It should thus exhibit a threshold behavior $\sigma(E) \propto E^{1/2}$ at near-zero electron energies [9,17], independent of the initial vibrational level ν of the F_2 molecule. Depending on the location of the $F_2{}^-(^2\Sigma_u{}^+)$ anion state [relative to the neutral $F_2(X\,^1\Sigma_g{}^+)$ potential energy curve] and on the coupling between the $e^- + F_2(X\,^1\Sigma_g{}^+)$ scattering states and the resonance state, the calculated DEA cross sections for $\nu = 0$ exhibit a maximum at energies of about 73 meV [14], 160 meV [13], and 250 meV [19]. For $\nu = 1$, the maximum shifts to higher energies in all calculations and exhibits a peak cross section which is a little higher than that for $\nu = 0$. For an ensemble of F_2 molecules at a vibrational temperature of $T_v = 300$ K (as relevant for the previous [5–7] and the present work) nearly all (98.6%) of the molecules reside in the lowest vibrational level $\nu = 0$; thus, the DEA cross section measured at or near $T_v = 300$ K largely reflects that for the vibrational ground state. We note that the calculated peak cross sections for $\nu = 0$ differ substantially [$(6–7) \times 10^{-20}$ m^2 [13,14] and 1.5×10^{-20} m^2 [19]].

The apparent discrepancy between the theoretical predictions [13,14,19] and the experimental observations [5–7] for the threshold behavior of the DEA cross section for F_2 is puzzling and has remained a challenge to date [8,17,20]. Several reasons for an s-wave threshold behavior have been proposed [7,8,13], including the nonadiabatic coupling between the $^2\Sigma_u{}^+$ and $^2\Sigma_g{}^+$ scattering states due to non-Born-Oppenheimer terms in the Hamiltonian. However, these interactions are expected to be small, and it appears unlikely that these effects could be observed. Experimentally, a measurement with sufficiently high resolution, low background, and a sufficiently well-characterized target gas sample is needed for a decisive result. In the present work we apply an improved version of the laser photoelectron attachment (LPA) method to restudy the energy dependence of the DEA cross section for F_2 at the well-defined gas temperature of 300 K over the electron energy range $E = 1–180$ meV. Our measurements exhibit a maximum in the F^- yield at $E \approx 31$ meV and a substantial drop toward lower electron energies. We interpret this finding as a clear demonstration of p-wave attachment near threshold in agreement with the theoretical predictions.

In order to measure highly resolved cross sections for anion formation in low-energy electron collisions with fluorine (F_2) molecules, we used an improved version of the LPA method [20,21]: energy-variable photoelectrons

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(current 20 pA, energy range 1–180 meV) were created in the reaction region with the target molecules by resonant two-color photoionization of ground-state potassium atoms [20,22]. A diffuse low-density target of 5% F_2 in helium (Linde Co.) at the gas temperature $T_G = 300$ K was used, and a pulsed sequence (100 kHz) of electron production and attachment followed by delayed anion extraction was applied. The anions resulting from attachment processes were mass selected with a quadrupole mass spectrometer and detected with an off-axis channel electron multiplier. A small background of F^- ions was observed which is attributed to the bimolecular reaction $F_2 + K_2 \rightarrow KF + K^+ + F^-$ [23], involving K_2 molecules which are present in the potassium beam at an estimated level of about 10^{-4}. In order to separate this background from the true signal due to reaction (1) the photoelectron production was periodically switched on and off for intervals of 10 ms each (identical to within 10^{-4}) and the respective anion counts stored separately. Typical counting rates amounted to 1/s for the background and 3/s for the maximum signal due to (1) at a partial F_2 pressure of about 2×10^{-6} mbar. The LPA-induced and the background F^- signals were found to rise linearly with target pressure. The F_2 and He components in the delivered gas mixture had specified purities of 99% and 99.999%, respectively. The data shown below were taken over a total sampling time of 21 h, following an initial passivation period of five days over which the energy dependence of the background-corrected F^- yield was found to vary. This behavior is attributed to the contribution of processes involving target gas components which are produced during the passivation period by reactions of the F_2 molecules with the gas-covered surfaces of the gas inlet system and the reaction chamber. The energy resolution in the F_2 experiment was assessed by comparing the well-known yield for SF_6^- formation [20,21,24] with that measured when a small amount of SF_6 gas was added to the vacuum chamber in the presence of the F_2-He mixture.

The background-corrected F^- yield is presented in Fig. 1. Most notably, one observes a rather steep rise from near-zero electron energy to a maximum at 31(2) meV, followed by a slower decrease toward higher energies. The increase at very low energies is compatible with p-wave threshold behavior. Note that the finite energy resolution (see below) causes a nonzero signal at threshold. Above 150 meV, the data appear to indicate—at somewhat higher scatter—a weak rise.

Another indication for the threshold behavior of the attachment cross section is provided by the energy dependence of the anion yield observed at negative energies, i.e., for Rydberg electron transfer (RET) processes. For Rydberg electron collisions the anion signal mirrors the RET rate coefficient k_{nl}. In the framework of the quasi-free Rydberg electron model [25,26] k_{nl} is given by $k_{nl} = \int \sigma(v) \cdot v \cdot f_{nl}(v) dv$, where v denotes the velocity and

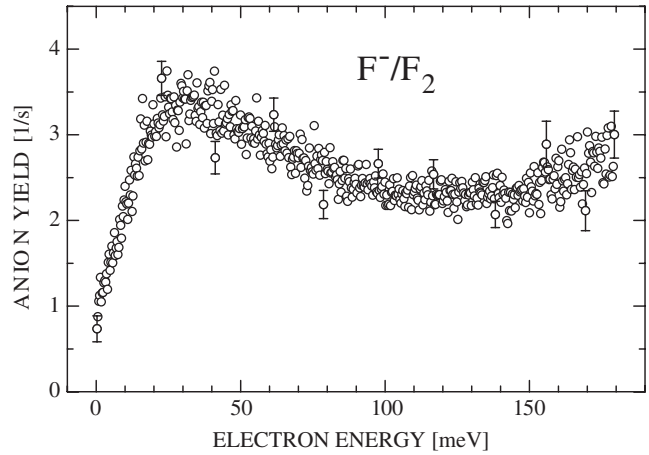

FIG. 1. Measured yield for F^- formation due to electron attachment to F_2 molecules.

$f_{nl}(v)$ denotes the normalized velocity distribution for the nl Rydberg electron. For sufficiently high principal quantum numbers ($n > 50$) postattachment interactions between the anion and the remaining positive ion core can be neglected [26]. Moreover, the electron velocities are so small that the attachment cross section can be replaced by its threshold velocity dependence; i.e. $\sigma_0(v) = c_0(v_0/v)$ for s-wave attachment and $\sigma_1(v) = c_1(v/v_1)$ for p-wave attachment with c_0, v_0 and c_1, v_1 constants. Thus, for s-wave attachment $k_{nl} = c_0 v_0$ is independent of n at high n, e.g., for SF_6^- formation from SF_6 [25,26]. For p-wave attachment, in contrast, one obtains $k_{nl} = (c_1/v_1) \int v^2 \cdot f_{nl}(v) dv = (c_1/v_1)\langle v^2 \rangle_{nl} = 2(c_1/v_1)|E_{nl}|/\mathrm{m}$, where E_{nl} is the (negative) binding energy of the Rydberg electron whose modulus is equal to the mean of its kinetic energy $\langle E_k \rangle_{nl} = (\mathrm{m}/2)\langle v^2 \rangle_{nl}$. In Fig. 2 we show the anion yields due to RET ($E < 0$) and due to free electron attachment for (a) F^-/F_2 and (b) SF_6^-/SF_6 over the electron energy range from $E = -3.8$ meV ($n = 60$) to $E = +14$ meV. The yield for SF_6^-/SF_6 formation (obtained in a single, short measurement at the end of the F_2 data runs) exhibits the expected s-wave behavior in the RET regime [25,26] (apart from the narrow transition region from Rydberg to free electron collisions) while the free electron anion yield at very low energies stays below that expected from the known cross section [21,24] (chain curve, normalized to the yield data at higher energies). We attribute this deviation to the finite resolution (estimated to be about 5 meV) due to the effects of residual electric fields. The RET-induced F^-/F_2 yield, on the other hand, decreases monotonically in a way which is essentially compatible with that predicted for p-wave attachment. The calculated RET rate coefficients (full curve: $l \ll n$; broken curve: fully l-mixed ensemble, jointly normalized to the respective anion yields) were obtained with analytical expressions for the free electron attachment cross sections [chain curves in Figs. 2(a) and 2(b)]; i.e.,

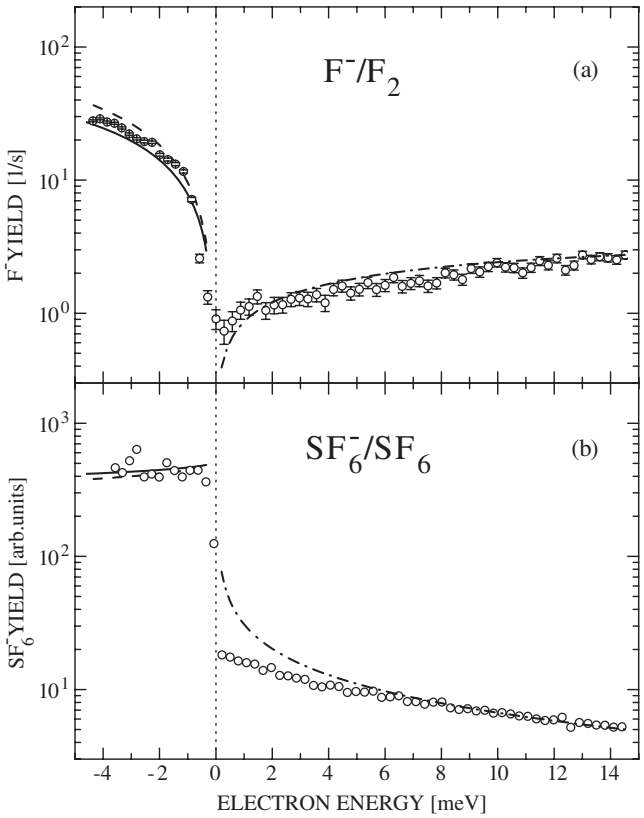

FIG. 2. Anion yields due to RET ($E < 0$) and free electron attachment ($E > 0$) for (a) F^-/F_2 formation and (b) $SF_6{}^-/SF_6$ formation. The full and broken curves represent RET rate coefficients calculated for Rydberg atoms with $l \ll n$ and a fully l-mixed ensemble (jointly normalized to the respective yields). For the chain curves, see the text.

for F^-/F_2, $\sigma(E) \propto E^{1/2}\exp[-E/E_1]$ with $E_1 = 73$ meV which represents a realistic fit to the measured yield up to $E = 100$ meV, and for $SF_6{}^-/SF_6$, $\sigma(E) \propto E^{-1}[1 - \exp(-0.405E^{1/2})]$, E in meV [21,24].

Thus, the experimental findings presented in Fig. 2 for the near-threshold energy dependence of F^- formation, both for RET at high n and for free electron attachment at very low energies, demonstrate p-wave threshold behavior in agreement with the p-wave character of the lowest anion resonance $F_2{}^-(^2\Sigma_u{}^+)$.

The observation of a peak at near-zero energy in the previous electron beam work on F_2 [5,6] can be explained by insufficient energy resolution (close to 0.1 eV). Chutjian and Alajajian [7], in contrast, used a VUV photoelectron method at distinctly lower energy width, involving photoionization of Kr atoms near the higher $Kr^+(^2P_{1/2})$ threshold in a gas mixture of 8% F_2 and 92% Kr. Their attachment line shapes for the F^- yield exhibited a spike at essentially zero electron energy with a width nearly equal to the optical resolution (6–12 meV) and a monotonic decrease toward higher electron energies (up to 140 meV). In the present LPA anion yield a "zero-energy spike" is absent. We tentatively attribute the findings in [7] to be due to the influence of RET-induced F^- formation involving long-lived highly excited $Kr^{**}(nl)$ Rydberg atoms below the $Kr^+(^2P_{1/2})$ threshold. Electric fields such as those used in [7] to continuously extract the anions produce long-lived autoionizing Rydberg states nl with high l by efficient l-mixing at a sufficiently high principal quantum number n. The relevant range of n corresponds to a narrow energy range close to the ionization limit and thus yields a resolution-limited spike just below threshold. Spikes of this origin have been observed in our LPA work involving photoionization of excited $Ar^*(4p\,^3D_3)$ atoms near the $Ar^+(^2P_{1/2})$ ionization threshold [21,27] (see Fig. 8 and the discussion in [27]).

The maximum in the LPA anion yield (see Fig. 1) occurs at a distinctly lower energy than in the calculations reported in [13,14,19]. To get more insight we carried out some exploratory R-matrix calculations of the DEA process. Using parameters that reproduce the anion curve and the adiabatic width of Bardsley and Wadehra [14] we obtained a DEA cross section which peaks at 170 meV. This is in contrast to the peak position of 73 meV, obtained by Bardsley and Wadehra, but not far from the results of Hazi *et al.* [13] and Brems *et al.* [19]. Note that the theoretical approach of Bardsley and Wadehra [14] is semilocal; i.e., it does not include the energy-dependent resonance shift due to the interaction between the diabatic state and the continuum. In contrast, the other two groups [13,19] used completely nonlocal theories.

When we modify the R-matrix surface amplitude to make it consistent with the width calculations of Ingr *et al.* [18], the maximum in the DEA cross section moves to 82 meV, but the peak value of the cross section drops substantially to 0.45×10^{-20} m^2, which is not consistent with the experimental estimates in [3,6,7]. All our attempts to modify the R-matrix parameters in such a way that the cross section would peak at a substantially lower energy led either to an anion potential curve, which was inconsistent with the known values of the electron affinity of F and of the dissociation energy of $F_2{}^-$, or to a cross section which is too small in absolute value. For example, a simple shift of the anion curve used by Bardsley and Wadehra to the left by 0.15 a.u. moves the peak position to 79 meV, but the cross section is reduced down to 0.042×10^{-20} m^2.

In contrast to the case of DEA to the Cl_2 molecule [28–30], the R-matrix theory or its equivalent, the nonlocal complex potential theory, thus appears to be unable to reproduce the location of the first maximum in the DEA cross section for F_2, observed at 31(2) meV in the present high resolution DEA experiment. We note that calculations within the local complex approximation [11] produced an artificial spike in the cross section at very low energies; however, as emphasized by Domcke [17], this approximation is not suitable for treating DEA to F_2 at very low energies. The direct (nonresonant) s-wave process dis-

cussed in the literature should be ruled out because the non-Born-Oppenheimer coupling cannot explain the large DEA cross section.

In conclusion, we emphasize again the important new finding of the present experiment, namely, that the cross section for electron attachment to F_2 at very low energies is dominated by p-wave threshold behavior. We can see no experimental artifact (such as impurities in the gas present in the reaction region) which would simulate p-wave behavior instead of s-wave-type behavior reported previously [6,7]. The observation of p-wave behavior is dictated by a special, selective symmetry of the target such as given here by the $^2\Sigma_u{}^+$ symmetry of the lowest anion resonance of F_2. It is expected that impurity molecules, formed by reactions of F_2 with adsorbates on walls, do not possess this special symmetry and thus should exhibit s-wave threshold behavior.

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