

Clear Experimental Evidence for p -Wave Attachment-Threshold Behavior in Electron Attachment to Chlorine Molecules

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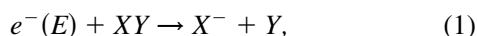
(Received 17 April 2002; published 2 August 2002)

Using the laser photoelectron attachment method and chlorine molecules in a seeded supersonic beam, we have measured the energy dependence of the cross section for dissociative electron attachment (DA; Cl^- formation) over the range 0–195 meV with an energy width of about 1 meV. Our data provide the first clear experimental evidence for p -wave behavior of a DA cross section near zero energy and are in good overall agreement with recent theoretical predictions.

DOI: 10.1103/PhysRevLett.89.083201

PACS numbers: 34.80.Ht, 34.10.+x

Attachment of low-energy electrons to molecules is an important process in gaseous dielectrics [1] and other environments including excimer lasers [2], discharges used for etching [3], and the earth's atmosphere [4]. Because of the high electron affinity of halogen atoms X , dissociative attachment (DA) to halogen containing molecules XY ,



may often occur with large cross sections $\sigma(E)$ down to zero electron energy, thus efficiently producing halogen anions as well as halogen atoms or halogen containing radicals which are important precursors for further reactions. In many cases s -wave capture is symmetry allowed and occurs with a cross section which rises strongly towards very low energies [$\sigma(E) \propto E^{-\kappa}$ with $0.5 \leq \kappa < 1$] [5–11].

One of the open problems in low-energy electron attachment studies is the threshold behavior for the anion yield in cases for which, based on the symmetry of the involved anion resonance state, s -wave electron attachment is forbidden. The C_{60} molecule was considered to be such a case for which the lowest unoccupied orbital in the C_{60}^- anion possesses ungerade symmetry compatible only with p -wave attachment [12], but recent work has demonstrated that besides p -wave also s -wave attachment (possibly mediated by phonons) occurs to a certain extent (see, e.g., [10]). A reliable theoretical prediction for the low-energy attachment behavior requires dependable *ab initio* calculations for the neutral and anion states which are involved in the attachment process. For the case of expected exothermic p -wave attachment, the only molecules which may be considered to fulfill this criterion are fluorine (F_2) and chlorine (Cl_2). Their neutral ground state has $1\Sigma_g^+$ symmetry [13]. The symmetry of the lowest anion states is $2\Sigma_u^+$, $2\Pi_{3/2,1/2g}$, $2\Pi_{3/2,1/2u}$, and $2\Sigma_g^+$ with general agreement that the ground anion state possesses $2\Sigma_u^+$ symmetry [13–16], as illustrated for the case of Cl_2 in Fig. 1. When the influence of states with $2\Sigma_g^+$ symmetry can be neglected at very low electron energies, anion formation

should be governed by p -wave attachment via the $2\Sigma_u^+$ state (note that s -wave attachment is not compatible with the ungerade symmetry of the $2\Sigma_u^+$ state) [17–19]. According to Wigner's threshold law [20], one thus expects a cross section rising as $\sigma(E) \propto E^{1/2}$ near zero energy. Such a behavior was predicted in theoretical calculations of DA cross sections for F_2 [17,18] and Cl_2 [21], but so far, a conclusive experimental confirmation of this prediction is missing. For F_2 , vacuum ultraviolet photoelectron attachment work (energy width ≤ 6 meV) [22] presented evidence for s -wave attachment, in line with previous evidence obtained with electron beams of much broader widths for both F_2 [23] and Cl_2 [24–26]. As cited in a review on electron interactions with Cl_2 [16], a recent high

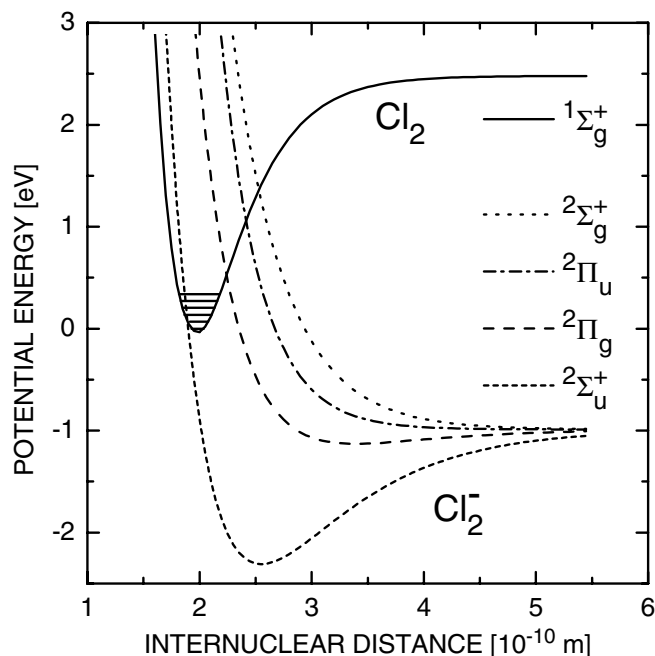
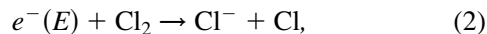


FIG. 1. Potential energy curves relevant for the dissociative electron attachment to $\text{Cl}_2(X^1\Sigma_g^+)$ molecules, drawn according to information in [13,15,16]. The influence of spin-orbit coupling on the anion curves is neglected.

resolution (≈ 60 meV FWHM) electron beam study of DA to Cl_2 between ≈ 0.0 and 0.7 eV ([27], Ref. [120] in [16], not published to date) showed two resonances at 0.03 and 0.25 eV; the former peak has been attributed to DA via the $^2\Sigma_u^+$ state of Cl_2^- . Swarm-unfolded cross sections have been reported for both F_2 [28] and Cl_2 [16,29], but the energy range does not extend to sufficiently low energies to allow conclusions on the threshold behavior of the cross section close to zero energy.

Because of the inconclusive experimental situation for this basic problem [7,19] and in view of the relevance of molecular chlorine as an etching gas [3] and a component of the perturbed chemistry of the polar stratosphere [4], we have carried out the first high resolution study of dissociative electron attachment to Cl_2 ,



over the electron energy range 0 – 200 meV. We use the laser photoelectron attachment (LPA) method [5,30,31] which we have developed over the last ten years and so far applied to investigate (dissociative) electron attachment to several molecules [5,8,11,32,33] and to molecular clusters [31,34,35] at unprecedented resolution. As long as residual electric fields are carefully controlled [5,8,30], effective electron energy widths around 1 meV and even as low as 20 μeV [8] are achieved. This is especially true when the target is prepared in a collimated molecular beam [8,31,34], thus leading to a spatially well-defined reaction volume over which the residual electric field can be easily minimized to values substantially below 1 V/m. It was thus possible to convincingly confirm the limiting behavior for s -wave electron attachment [$\sigma(E) \propto E^{-1/2}$] [5,8,33], to detect cusps in the attachment cross sections at onsets for vibrational excitation [5,11,32,33] and to observe narrow vibrational Feshbach resonances (width down to 2.3 meV [34]) in electron attachment to molecules [32] and molecular clusters [34,35]. In the present Letter, we report relative cross sections for Cl^- formation due to laser photoelectron attachment to Cl_2 molecules, seeded in a supersonic beam of helium atoms at a source temperature of 500 K. Our data, obtained in a difficult measurement over the electron energy range 0 – 195 meV at an energy width of about 1 meV, provide the first clear experimental evidence for p -wave behavior of the DA cross section at very low energies and are found to be in very good overall agreement with recent calculated cross sections [21].

Our experiment is sketched in Fig. 2. Energy-variable, monoenergetic electrons (current 30 pA) are created by photoionization of $^{39}\text{K}^*(4p_{3/2}, F = 2, 3)$ atoms [prepared by excitation of $^{39}\text{K}^*(4s, F = 1, 2)$ atoms in a collimated potassium beam with a two-frequency laser at $\lambda_1 = 766.7$ nm [31]] with the intracavity field of a broadband (40 GHz) tunable dye laser (power up to 5 W), operated in the blue spectral region ($\lambda_2 = 472$ – 424 nm, dye Stilbene 3). The energy E of the photoelectrons can be continuously varied over the range 0 – 200 meV by tuning the wavelength

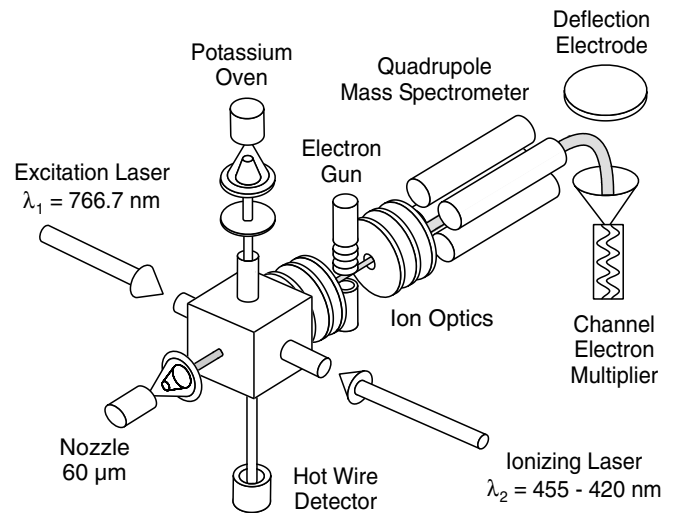


FIG. 2. Semischematic view of the laser photoelectron attachment apparatus.

of the ionizing laser ($\lambda_2 < 455$ nm). The photoelectrons may attach to molecules in a collimated, differentially pumped, seeded supersonic beam (4.6% Cl_2 in helium; diameter in the reaction region 3 mm; nozzle diameter $d_0 = 60$ μm , stagnation pressure $p_0 = 1$ bar, and nozzle temperature $T_0 = 500$ K), propagating in a direction perpendicular to both the potassium and the laser beams. Anions, generated by electron attachment and drifting out of the essentially field-free reaction chamber, are imaged into a quadrupole mass spectrometer ($m/q \leq 2000$ u/e) with a combination of two electrostatic lenses. The transmitted ions are accelerated to an energy of 1 keV and detected by a differentially pumped off-axis ceramic channel electron multiplier with very low dark counts (< 0.02 s^{-1}).

The reaction volume is surrounded by a cubic chamber, whose inner walls are coated with colloidal graphite. By applying bias potentials to each face of the cube, dc stray electric fields are reduced to values $F_S < 0.1$ V/m. Magnetic fields are reduced to values below 2 μT by compensation coils located outside the vacuum apparatus. The electron energy resolution is limited by the bandwidth of the ionizing laser ($\Delta E_L \approx 0.15$ meV), residual electric fields ($\Delta E_F \leq 0.3$ meV), the Doppler effect, present in both the photoionization and in the attachment process (overall Doppler width $\Delta E_D \approx 0.18\sqrt{E}$ for Cl_2 seeded in He at $T_0 = 500$ K, ΔE_D , and E in meV), and space charge broadening ΔE_{SC} due to the K^+ photoions generated in the reaction volume ($\Delta E_{SC} \approx 0.9$ meV at 30 pA photocurrent; see Fig. 7 in [36]). For the sake of normalization, *in situ* resolution testing and compensation of electric stray fields, measurements of SF_6^- formation were frequently carried out, using a seeded supersonic beam of about 0.05% SF_6 in He ($p_0 = 1$ bar, $T_0 = 300$ K). By comparison of the measured anion yield with the known cross section for SF_6^- formation [5,8,30] near 0 eV (convoluted with adjustable resolution functions), the effective electron energy spread

at low energies can be inferred. From this comparison (and compatible with the information gained on the energy broadening due to the photoion space charge [36]), we estimate the overall energy spread (FWHM) at low energies to be about 1 meV for the conditions of the presented measurements. Towards higher energies, the spread will increase due to the Doppler effect and reach almost 3 meV at the highest energies.

The use of the seeded supersonic beam with helium as carrier gas leads to a substantial increase in the velocity of the Cl_2 molecules above its thermal value, which results in a higher detection efficiency of the Cl^- product ions under conditions of weak extraction fields. Since we are mainly interested in the energy dependence (i.e., the shape) of the DA cross section, the important issue is the variation of the ion detection efficiency over the electron energy range of interest (0–200 meV). Estimates show that the Cl^- detection efficiency drops by about 8% over this energy range; the raw data have been corrected accordingly.

A question of major concern in the present experiment is the amount of spurious Cl^- ion production due to chlorine clusters in the seeded supersonic beam as well as heavy particle collisions of Cl_2 molecules with K_2 molecules [37], present at a small concentration in the potassium beam. Thus, extensive series of test measurements (to be described elsewhere) were carried out. Cluster formation was studied by measuring mass spectra due to electron impact ionization with an auxiliary electron gun (see Fig. 2) for several nozzle temperatures and stagnation pressures. At $p_0 = 1$ bar and $T_0 = 500$ K (used for the attachment data shown below), the $\text{Cl}_4^+/\text{Cl}_2^+$ intensity ratio amounted to 0.0004 from which we can infer (using the fragmentation pattern of O_2 dimers [38]) that the dimer density is only about 1% of the Cl_2 monomer density. In the absence of both lasers, the exothermic bimolecular reaction $\text{K}_2 + \text{Cl}_2 \rightarrow \text{K}^+ + \text{Cl}^- + \text{KCl}$ [37] was in fact observed for typical conditions of the two-chamber potassium oven, yielding a Cl^- count rate of about 4 s^{-1} . With the infrared laser on resonance and the blue laser tuned *in between* clearly separated Rydberg states below the ionization threshold (to test, e.g., for the possible effect of electrons created at surfaces by stray photons), the Cl^- intensity did not change. When the infrared laser (λ_1) was on resonance and the blue laser tuned into the ionization continuum, producing photoelectrons with energies around 50 meV (the expected position for maximum free electron attachment to Cl_2 [21]), a weak rise in the Cl^- signal (corresponding to a net additional counting rate of about 0.85 s^{-1}) was reproducibly observed which we attribute to the dissociative attachment process (2). Since we had no option to remove or substantially decrease the background Cl^- signal due to the bimolecular reaction, we decided to carry out a large number of repeated scans over the electron energy range from -3 to $+202$ meV. At the used laser bandwidth of 0.15 meV, free electron data ($E > 0$ meV) were found to be influenced by signals due to Rydberg electron transfer ($E < 0$ meV) for energies up to $E =$

$+0.25$ meV. For electron energies 195–202 meV, the blue ionizing laser was interrupted in each run, thus creating a background signal to be subtracted from the anion intensity obtained with the blue laser in operation. The data were taken with a channel width of about 0.12 meV and summed over long periods of time (total data accumulation time about 400 h).

The relative DA cross section (Cl^- yield) obtained over the range 0.6–195 meV is presented in Fig. 3 (open circles, channel width 0.6 meV by averaging over five adjacent data points). Above zero energy the cross section rises sharply, reaches a maximum around $E = 50$ meV, and then decreases monotonically and without any significant structure. At $E = 180$ meV the DA cross section is down from the peak value by a factor of 3.4. The full line in Fig. 3 is the theoretical prediction of Fabrikant *et al.* [21], normalized to the experimental data at the maximum. This theoretical cross section (peak value $2.60 \times 10^{-20} \text{ m}^2$) was calculated as the sum over the contributions from the different initial vibrational levels $\nu_i = 0-3$ with weights according to their thermal population at a temperature of $T_i = 500$ K. This choice for T_i is not critical for the comparison: calculations with lower temperatures yield smaller absolute values of the cross section (see the dashed line in Fig. 3 for $T_i = 300$ K; peak value $1.75 \times 10^{-20} \text{ m}^2$) but essentially the same cross section shape. The energy dependence of the measured cross section is found to be in very good agreement with the theoretical prediction [21].

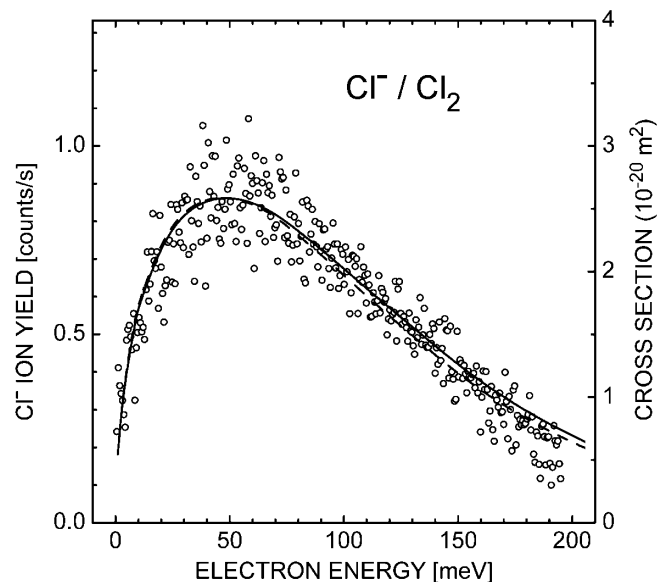


FIG. 3. Cross section for dissociative electron attachment to $\text{Cl}_2(X^1\Sigma_g^+, \nu_i)$ molecules. Open circles: LPA results, averaged over five adjacent data points, corresponding to a channel width of close to 0.6 meV and a measurement time per shown channel of about 4000 s. Full line (dashed line): calculated DA cross section for a vibrational temperature of $T_i = 500$ K ($T_i = 300$ K), as normalized to LPA data at the maximum. The absolute cross section scale is relevant for the calculation at $T_i = 500$ K.

The steep rise above zero energy is characteristic for p -wave attachment which to our knowledge is here experimentally demonstrated for the first time in a clear and convincing way. In accord with the theoretical prediction, the sharp rise levels off rapidly; this is due to the fact that the Franck-Condon factor between the vibrational levels in the neutral and the anion state drops quickly with rising electron energy in this case [21]. The small DA anion signals are consistent with an absolute peak cross section in the low 10^{-20} m² range, as coarsely estimated through a comparison of the positive ion signals due to electron impact ionization (for its cross section, see [16]) and the weak Cl⁻ signal due to dissociative attachment. Our data—as well as the theoretical results—show no evidence for structure in the DA cross section which could be related to features, recently observed in the total scattering cross section of Cl₂ over the range 70 to 180 meV [39].

A detailed account of the present work will be presented elsewhere. In future work it would be of interest, also in connection with recent high level calculations of the lowest F₂⁻ resonance state [14], to restudy the threshold behavior of electron attachment to F₂ molecules at meV energy width in order to clarify the existing discrepancy [19] between theory [17,18] and experiment [22].

This work has been supported by the Deutsche Forschungsgemeinschaft through Forschergruppe *Niederenergetische Elektronenstreuprozesse* and by the Zentrum für Lasermesstechnik und Diagnostik at Universität Kaiserslautern. We gratefully acknowledge I. I. Fabrikant for discussions and for providing calculated cross sections in numerical form. We thank L. S. Cederbaum, H. D. Meyer, and T. Sommerfeld for insightful discussions on resonances in the halogen dimer anions and the authors of [27] for providing a preprint.

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