Experimental SF_6^-/SF_6 and $Cl^-/CFCl_3$ Electron-Attachment Cross Sections in the Energy Range 0-200 meV

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Experimental cross sections for the electron-attachment processes for SF_6^-/SF_6 and $Cl^-/CFCl_3$ are reported in the energy range 0–200 meV by normalizing each attachment line shape to measurement of a thermal rate coefficient. When the same ion states are detected, good agreement is found between present values, for which a monoenergetic electron source is used, and swarm-unfolded results. The present data constitute a new limit for cross sections reported at high resolution at the lowest electron energy.

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The attachment of low-energy electrons to species such as SF_6, $CFCl_3$, and perfluorinated carbon compounds (PFC's) has been the subject of two confluent streams of research. One approach deals with the electron attachment properties of SF_6 and the PFC's with the goal of improving high-voltage-breakdown properties of gases.[1-3] The other approach deals with the idea that a high-Rydberg electron is a "free" electron,[4] and that one may obtain electron-attachment cross sections from collisional ionization rates.[5-7]

In this Letter we report absolute electron-attachment cross sections for SF_6 and $CFCl_3$ by the TPSA (threshold photoelectron spectrum by electron attachment) technique.[8,9] Here, a mixture of Xe atoms and SF_6 molecules in a concentration ratio of about 7:1 is photoionized. One generates thereby *in situ* a narrow band of low-energy electrons by photoionization to the $^2P_{1/2}$ level of Xe^+; that is $Xe(^1S_0) + \hbar\omega \rightarrow Xe^+(^2P_{1/2}) + e$ (energy ϵ). The electrons e then attach to the admixed SF_6 to form SF_6^-. The SF_6^- ions are drawn out of the collision region, mass analyzed, and their signal detected as a function of the photoionization energy $\hbar\omega$. The electron energy is continuously variable from 0 meV (at the $^2P_{1/2}$ threshold) to, in this study, 200 meV.

Line shapes for electron attachment to SF_6 and $CFCl_3$ were reported earlier.[9] In addition to the repeller-box study in that work, further tests were carried out here to ensure that the measured line shapes were independent of pressure, and of voltages on ion-drawout lenses exterior to the collision box. For both attaching gases the dependence of ion signal on pressure of the major Xe component was studied in the range from 1.0×10^{-3} to 7.5×10^{-5} Torr at an energy corresponding to the peak of the profile, and to a point approximately one-third the peak height. In the four measurements the signal was found to vary linearly with Xe pressure to within an uncertainty of 5%. In addition, many variations of lens voltages were tried, and the SF_6 linewidth measured. The minimum width was found to be the 33 meV reported earlier.[9] Also, one notes that the attachment shapes in both SF_6 and $CFCl_3$ rise from onset to peak within about 8 meV.[9] The stray-field width in the collision chamber must be less than this, since a portion of that 8 meV width arises from the photon bandwidth.

The relative line shapes can be converted to absolute cross sections in either of two distinct ways. In one, a thermal attachment rate coefficient[10,11] k can be used as a source of calibration by the definition

$$k(\langle\epsilon\rangle) = (2/m)^{1/2}\int_0^\infty \sigma_A(\epsilon)\epsilon^{1/2}f(\epsilon)d\epsilon \ \text{cm}^3/\text{s}, \qquad (1)$$

where m is the electron mass, $\sigma_A(\epsilon)$ the electron-attachment cross section, and $f(\epsilon)$ a Maxwellian electron-energy distribution at the mean energy $\langle\epsilon\rangle$ corresponding to the SF_6 or $CFCl_3$ temperature (usually 300 K). In the second approach use is made of SF_6^-/SF_6 or $Cl^-/CFCl_3$ electron-attachment cross sections at higher energies ($\epsilon \geq 40$ meV) which have been unfolded from swarm-measured attachment rates.[1-3] These cross sections serve as calibration points for placing the entire range of $\sigma_A(\epsilon)$ on the absolute scale.

We opt for the first method of calibration because (a) the attachment rate k in Eq. (1) is accurately known for SF_6 and $CFCl_3$, and (b) the assumption of a Maxwellian distribution having been attained at a fixed gas temperature seems to us to be less ambiguous than results of a swarm-unfolding procedure in which the cross section depends strongly upon the calculated electron-energy distribution of the swarm (see below).

From earlier results[9] the measured production yield $P(E_0)$ of ions can be written as the convolution of the spectrometer slit function S with the product of the attachment cross section $\sigma_A(\epsilon)$ and the Xe photoionization cross section σ_I, or

$$P(E_0)=\int_0^\infty S(E_0-E_t-\epsilon)\sigma_I(E_t+\epsilon)\sigma_A(\epsilon)d\epsilon, \qquad (2)$$

where E_t is the $\mathrm{Xe}^+({}^2P_{1/2})$ photoionization threshold energy (13.436 eV) and E_0 the incident photon energy at the center of the bandpass.

In practice, two exponential slopes[12] γ_1 and γ_2, each over a separate energy range, were used to fit the observed[9] $P(E_0)$, so that $k(\langle\epsilon\rangle)$ contained contributions from each range. If we assume the form $\sigma_A(\epsilon)\sim\exp(-\epsilon/\gamma_i)$, and a Maxwellian distribution for $f(\epsilon)$ given by

$$f(\epsilon)=(2/\sqrt{\pi})(3/2\langle\epsilon\rangle)^{3/2}\epsilon^{1/2}\exp(-3\epsilon/2\langle\epsilon\rangle),$$

integration of Eq. (1) can be carried out by parts to give

$$k(\langle\epsilon\rangle)=[(1.233\times10^8\sigma_0)/\langle\epsilon\rangle^{3/2}]\sum_{i=1}^{2}a_i\,\Gamma_i^{\,2}[(1+\epsilon/\gamma_i)\exp(-\epsilon/\Gamma_i)]_{\epsilon_{ui}}^{\epsilon_{li}}, \qquad (3)$$

where ϵ_{li} and ϵ_{ui} refer to lower and upper energies in each range i. The limits ϵ_{l1} and ϵ_{u2} were, respectively, zero and infinity by Eq. (1). The intermediate limit ϵ_{l2} $(=\epsilon_{u1})$ was just the matching point of the two experimental pieces. It, as well as the slopes γ_1 and γ_2, and the relative amplitude a_2 of the two exponential sections $(a_1=1.0)$ were computed by an exponential curve fitting to $P(E_0)$ in Eq. (2). The resultant fit was within the statistical error in $P(E_0)$ except in the range 0–6 meV where the fit lay 10% below the data. (Use of a third exponential in this range would improve agreement. However, this was not done in light of the uncertainties involved at $\epsilon\lesssim4$ meV.) The normalization constant to the absolute cross-section scale is just σ_0.

Results of the fit for the $\mathrm{SF_6^-/SF_6}$ and $\mathrm{Cl^-/CFCl_3}$ attachment processes are, respectively, the following:

$$\sigma(\epsilon)=5.20\times10^{-14}\times\begin{cases}\exp(-\epsilon/44.4)\ \mathrm{cm}^2, & 0\leq\epsilon\leq45\ \mathrm{meV}\\ 0.868\exp(-\epsilon/51.6)\ \mathrm{cm}^2, & 45\leq\epsilon\leq200\ \mathrm{meV},\end{cases} \qquad (4)$$

$$\sigma(\epsilon)=3.36\times10^{-15}\times\begin{cases}\exp(-\epsilon/34.9)\ \mathrm{cm}^2, & 0\leq\epsilon\leq63\ \mathrm{meV}\\ 0.569\exp(-\epsilon/50.7)\ \mathrm{cm}^2, & 63\leq\epsilon\leq200\ \mathrm{meV}.\end{cases} \qquad (5)$$

The values of $k(\langle\epsilon\rangle)$ used in the calibration were[11] 2.28×10^{-7} cm^3/s with an estimated uncertainty of less than 5% for $\mathrm{SF_6}$, and[3] $(1.21\pm0.12)\times10^{-8}$ cm^3/s for $\mathrm{CFCl_3}$, with $\langle\epsilon\rangle=38.8$ meV (300 K). Results for $\mathrm{SF_6}$ and $\mathrm{CFCl_3}$ are shown in Figs. 1 and 2, respectively. In both cases $\sigma_A(\epsilon)$ is found to be a maximum at 0 meV, to within an experimental uncertainty of 4 meV at threshold. The shaded regions represent uncertainties due to (a) statistical error in $P(E_0)$, (b) error in the measurement of $k(\langle\epsilon\rangle)$, and (c) error in the fit to $P(E_0)$. These were combined in quadrature to give overall errors (12–18)% (for $\mathrm{SF_6^-/SF_6}$) and (15–18)% (for $\mathrm{Cl^-/CFCl_3}$), where the smaller error refers to the range 0–60 meV, that error increasing linearly to the larger value at 200 meV.

In Fig. 1 the present results are compared to the data of Christodoulides *et al.*[2] and McCorkle *et al.*[3] The last two sets of cross sections were unfolded from the same swarm attachment rates.[1] Differences between the two sets, in both magnitude and shape, lie in the use of different electron-energy distribution functions for $\mathrm{N_2}$.[3, 13] Good agreement is seen between the TPSA and newer swarm cross sections. The present measurements provide new data in the region $0\leq\epsilon\leq10$ meV, and the fact that $\sigma_A(\epsilon)$ has its maximum within 4 meV of 0 meV has important consequences for the temperature dependence of the attachment rate coefficient.[11] Attachment cross sections are also given by Kline *et al.*[14] These cross sections are in somewhat better agreement with data based on the newer $\mathrm{N_2}$ distribution function[3] (Fig. 1, open circles), and with the present results.

The differences of the present data with the swarm-unfolded cross sections[2, 3] point up an important result of this work, namely that the present $\sigma_A(\epsilon)$'s do not require a solution of Boltzmann's equation for obtaining a swarm electron-energy distribution function. One need only assume that a Maxwellian distribution has been attained at 300 K in the attachment-rate measurements.[10, 11] Even this assumption is not overly critical. For example, one may use a Druyvesteyn[15] form for $f(\epsilon)$ in Eq. (1), and carry out the integration in terms of error functions. The value of σ_0 obtained now is 0.76 times that of the Maxwellian case, indicating an insensitivity of

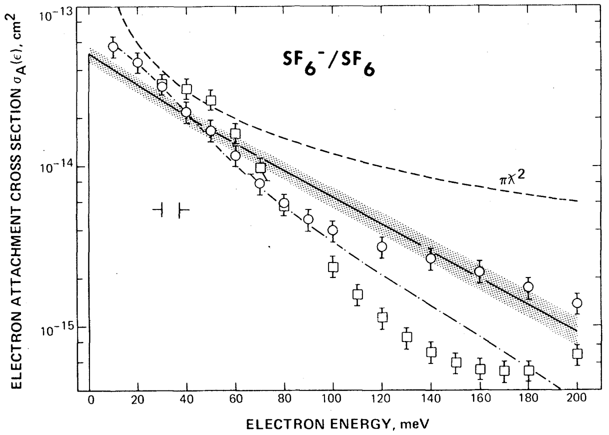

FIG. 1. Electron-attachment cross sections for SF_6. Present experimental measurements are given as the solid line with errors indicated by shading. Open squares are swarm-unfolded measurements of Christodoulides *et al*. (Ref. 2) and open circles are those of McCorkle *et al*. (Ref. 3), which use two different electron-energy distributions. These data include production of all negative ions from SF_6, in addition to SF_6^-. Results of Kline *et al*. (Refs. 12 and 14) (dot dashed line) are accurate for energies $\epsilon \geq 100$ meV, but the shape in the range $10 \leq \epsilon < 100$ meV is instrumental. Also shown are the electron energy resolution in the present data, and the maximum *s*-wave capture cross section $\pi\bar{\lambda}^2$ (dashed line).

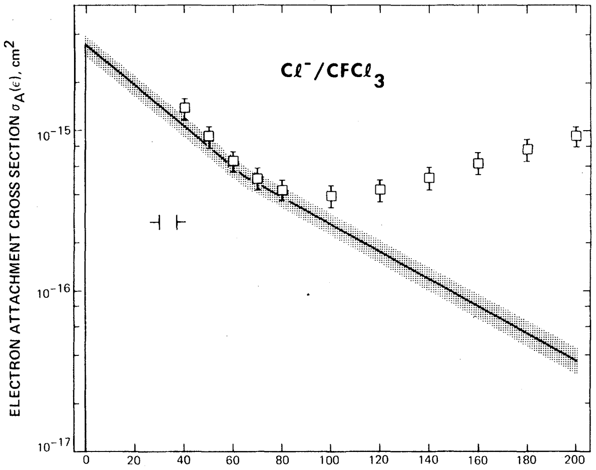

FIG. 2. Electron-attachment cross sections for $CFCl_3$. Present results are given as the solid line with errors indicated by shading. Open squares are swarm-unfolded data of McCorkle *et al*. (Ref. 3) for the production of all negative ions. The difference between the two sets of data at $\epsilon \geq 100$ meV arises from channel(s) for negative-ion production other than for $Cl^-/CFCl_3$.

$\sigma_A(\epsilon)$ to the form of $f(\epsilon)$, relative to the dependence of swarm values[2,3] on requirements and assumptions (necessary cross sections, two-term versus multiterm solutions) incurred by a Boltzmann-equation approach.

New data for the region $0 \leq \epsilon < 40$ meV are given for the attachment process for $Cl^-/CFCl_3$ in Fig. 2, and compared with swarm results of McCorkle *et al.*[3] We note here, however, that the magnitudes of the TPSA and swarm cross sections at the lower energies ($\epsilon < 100$ meV) are not strictly independent, since the thermal rate of McCorkle *et al.*[3] was obtained by averaging their swarm-unfolded cross sections with a Maxwellian $f(\epsilon)$, whereas for SF_6 it was derived from a $k(\langle\epsilon\rangle)$ measured in a separate experiment.[10, 11] However, these results demonstrate another principal feature of the TPSA method in that $\sigma_A(\epsilon)$ in both Figs. 1 and 2 refer to a *particular channel* for negative-ion formation. That channel is SF_6^- from SF_6 in Fig. 1, and Cl^- from $CFCl_3$ in Fig. 2. The swarm-unfolded data reflect *all open channels* for attenuation of the electron swarm. For energies $\epsilon < 100$ meV, the swarm and TPSA data refer to the same channels since the thermal electron attachment process is predominant. At larger energies, one can expect other channels to contribute to the swarm-unfolded data but not to the TPSA data. For example, the SF_5^-/SF_6 process starts at thermal energies,[16] and attains a broad maximum at[1] 0.35 eV. This is probably the reason for the slower falloff in the swarm data at $\epsilon > 100$ meV in Fig. 1. Likewise, a new channel is almost certainly responsible for the increase in negative-ion production in $CFCl_3$ (Fig. 2) for $\epsilon > 100$ meV. From our results, we conclude that this new channel *cannot* be Cl^- formation as found by Curran,[17] but rather to some other negative ion from $CFCl_3$.

The present results appear to have some relevance to the study of collisional ionization of high-Rydberg (HR) atoms by SF_6.[4-7] From Matsuzawa's theory,[4] the *rate constant* (i.e., cross section averaged over a velocity distribution of the colliding partners) for ionization of a HR atom should be equal to that of attachment of the "nearly free" HR electron to the attaching partner. This rate correspondence has been demonstrated by Foltz *et al.*[6] and Dimicoli and Botter.[7] Cross sections have been reported[5-7] by dividing the rate constant by some average relative velocity of the colliding partners. These cross sections, of the order 10^{-12} cm^2, have been somewhat loosely referred to as attachment cross sections (see, for example, the abstract of Ref. 4) since a HR electron is "nearly free." The present results indicate that the maximum cross section for attachment in which the electron is *truly* free is 5.20×10^{-14} cm^2 for SF_6^-/SF_6, and 3.36×10^{-15} cm^2 for $Cl^-/CFCl_3$. These are 10^{-2}–10^{-3} the reported collisional ionization cross sections.

However, the idea of a HR electron behaving as a free electron is somewhat unsatisfying on a simple energetic principle. One has to overcome the binding energy (5–50 meV, say) of that electron relative to its core. Indeed, recent experiments[7] have shown that this binding energy has to be taken into account, and that the positive-ion core does play a role in the electron transfer. Such core effects are absent in the TPSA technique, thus in the $\sigma_A(\epsilon)$ reported here.

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