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Statistical electron emission after laser excitation of C_{60}^{-} ions from an electrospray source

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We have measured electron emission from C_{60}^{-} ions in a storage ring. The ions were produced at room temperature and excited by absorption of photons with a total energy of 14 eV. The observed lifetime (~ 0.6 ms) is consistent with detailed balance and a cross section of 42 Å^2 for electron attachment. The measurements also determine the thermal radiation intensity I_r at a well-defined internal temperature T, $I_r = 138 \pm 20$ eV/s at $T = 1356$ K. The results are consistent with the scaling law $I_r \propto T^6$ and with the intensity, $I_r \sim 200$ eV/s at 1400 K, inferred from previous measurements of cooling in a storage ring of C_{60}^{-} ions injected from a hot source.

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I. INTRODUCTION

Central for the interpretation of delayed electron emission from excited clusters or molecules is the question whether the system has reached an internal equilibrium before the decay. Fullerenes play a special role in the study of this question owing to the many measurements of both attachment and emission of electrons, and of the competing deexcitation by photon emission. For fullerene anions, early measurements of emission rates after excitation by scattering from a solid surface seemed to indicate that the process is nonergodic [1], but this interpretation has recently been challenged [2]. The emission rate in equilibrium may via the detailed-balance relation be expressed in terms of the cross section for electron attachment [2], and in experiments with crossed beams of electrons and of fullerene molecules from an oven, both attachment cross sections and emission rates can be measured [3–5]. The results confirm the assumption of statistical equilibrium within the uncertainty of the measurements [2], but this uncertainty is rather large, partly because the molecules are produced in an oven with a considerable spread in internal energy. It may also be argued that electron attachment populates the part of phase space, which is strongly coupled to electron emission, and that it is an open question whether excitation by different means leads to decay with the same lifetime.

We describe measurements with room-temperature C_{60}^{-} ions excited by photon absorption. The ions were produced by an electrospray source and stored for tens of milliseconds in a Paul trap with a room-temperature buffer gas. They were then ejected and, after acceleration and magnetic analysis, injected into an ion storage ring. Here they were excited by absorption of higher-harmonic photons from a Nd:YAG laser, and the decay by electron emission was followed in time by detection of neutral molecules. We have identified a signal from absorption of three fourth-harmonic photons, corresponding to a total photon energy of about 14 eV, and have obtained the lifetime for a well-defined excitation energy. Together with the earlier results for emission after electron attachment, this measurement tests that the rate of electron emission is independent of the excitation mechanism, and it gives an independent determination of the pre-exponential frequency factor in the Arrhenius decay law. The same excitation energy was reached by absorption of four third-harmonic photons and of six second-harmonic photons. In all cases a significant tail of the decay curve is observed, which corresponds to absorption of one photon less. Because the lifetime is considerably longer, it is strongly influenced by radiative cooling of the molecules [6–8], and in contrast to earlier experiments, the measurements determine the cooling rate for an excitation energy given directly by the experimental parameters.

II. EXPERIMENT

The experimental arrangement is described in detail in Ref. [9]. The fullerene ions are produced in an electrospray ion source, as illustrated in Fig. 1. The spray solution consists of 50 μl of a solution of C_{60} (1 mM) in toluene, mixed with 50 μl of a solution of tetrathiafulvalene (TTF) (1 mM) in dichloromethane and diluted with dichloromethane to 1 ml. TTF acts as an electron donor with C_{60} as an acceptor since the TTF/TTF$^+$ redox potential (0.38 V vs Ag/AgCl) is higher than that of C_{60} /C_{60}^{-} (-0.80 V vs Ag/AgCl) [10,11]. The solution is sprayed through a needle at -4 kV with a flow rate of 4 μl/min. The C_{60}^{-} ions are liberated from the solvent during passage through a thin

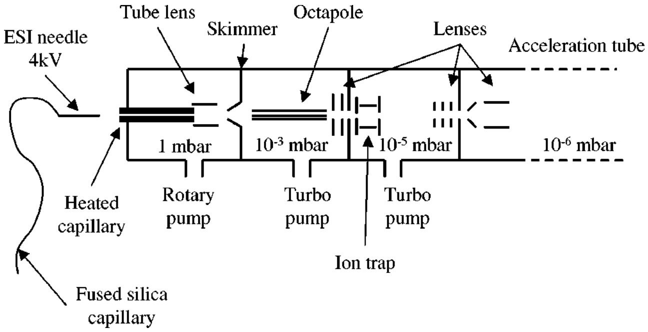

FIG. 1. Electrospray source. The solution is sprayed at atmospheric pressure, and in the heated capillary the solvent in the small charged droplets is evaporated. The ions are guided by electric fields into the ion trap with a buffer gas at $1/10^{-3}$ mbar. A positive potential at the skimmer stops the loading of the trap at a variable time, 10–80 ms before ion ejection into the acceleration tube.

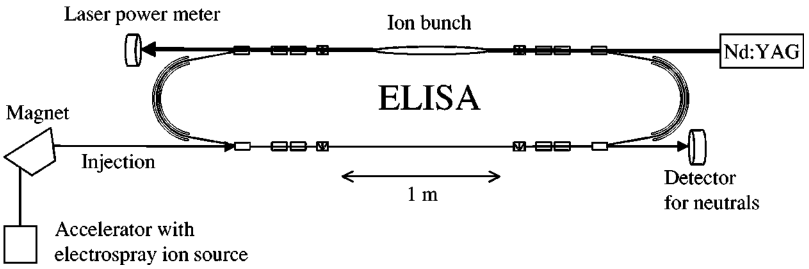

FIG. 2. The electrostatic storage ring ELISA. A bunch of ions is injected from the lower left and neutrals are detected from each passage of the lower straight section. The ions can be excited by a laser beam in the upper straight section.

heated capillary (180 °C) into a first chamber, pumped down to about 1 mbar, and are guided by the electric field from the tube lens through a skimmer into a second chamber with a pressure of about 10^{-3} mbars. Here the motion is confined by an octapole beam guide, and the ions pass through a lens system into a third chamber at about 10^{-6} mbars, where they are stored in a Paul trap with a He buffer gas maintained at about 10^{-3} mbars with an adjustable gas inlet. With a repetition rate of 10 Hz, the ions are ejected from the trap and focused by an Einzel lens into the acceleration tube of an isotope separator.

After acceleration to 22 keV and magnetic separation, the ions are injected as a short pulse into the electrostatic storage ring ELISA [12], as illustrated in Fig. 2. The pressure in the ring is so low (a few times 10^{-11} mbars) that a negligible fraction of the ions are lost by collision with the rest gas during the ~16 ms of observation. A few milliseconds after injection, the ions are illuminated in one side of the ring with a pulse of second, third, or fourth harmonic radiation from a Nd:YAG laser, and subsequently the neutral molecules created by delayed electron emission in the other side of the ring are detected with a micro-channel-plate detector. The solid angle covered by this detector is large enough to capture nearly all the neutral C_{60} molecules produced in the straight section between the end deflections of the beam, but betatron oscillations of the beam lead to small fluctuations (~20%) in the count rate because there is a variation of the detection efficiency over the surface area of the detector.

A spectrum recorded after illumination with a single pulse of fourth-harmonic radiation is shown in Fig. 3. The revolution time in the ring is 108 μs, and neutrals produced by electron emission are detected each time the short ion bunch (~5 μs) passes the detector. The yield of neutrals increases dramatically after the laser illumination at 4.3 ms and then decays nearly exponentially. The measurement covers a time variation of about two orders of magnitude, and within this time window the yield is dominated by the contribution from absorption of three photons. We have determined this number by observation of decay with the same lifetime after illumination with third-harmonic radiation (four-photon absorption). The excitation energy must be the same in the two measurements, i.e., the total photon energy absorbed must be an integer times $4\times3\times1.165$ eV$=14.0$ eV. The value 14 eV is confirmed by the consistency with other experiments, as discussed in the analysis below.

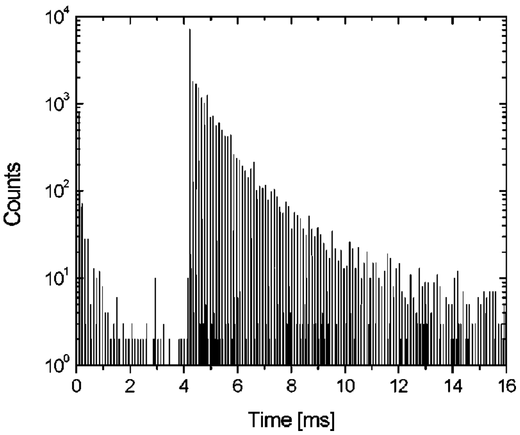

FIG. 3. Time spectrum of the counts of neutrals, with excitation at 4.3 ms by fourth-harmonic radiation from a Nd:YAG laser. The separation of the peaks corresponds to the revolution time, 108 μs.

Owing to the large heat capacity of C_{60}, the control of the initial temperature is very important. When the ions are stored for tens of milliseconds in the Paul trap, they should reach an equilibrium with the room-temperature helium gas. However, there is a risk of filling too many ions into the trap. The Coulomb repulsion leads to expansion of the ion cloud with increasing number of ions, and the C_{60}^- ions may be pushed out from the center of the trap because the effective confining field in an rf trap is stronger for lighter ions. Since the rf field increases with the distance from the effective potential minimum in the center of the trap, the micromotion of the ions can then induce an internal heating by gas collisions [13]. In an earlier experiment, a significantly shorter lifetime was observed, which may be explained by heating to about 400 K in the trap. We have, therefore, introduced a positive potential at the skimmer, cutting off the trap filling 10–80 ms before ion ejection. This procedure also ensures that all ions have been stored in the trap in contact with the buffer gas for at least 10 ms. We checked that the lifetime of the decay by electron emission after laser excitation was independent of the filling time. In the spectrum shown in Fig. 3 there is a small yield just after injection, which probably stems from a small fraction of very hot molecules. Since the internal energy must be quite large, of order 15 eV or more, we believe that this heating must be due to single collisions with rest gas molecules in the acceleration region, and we have observed a correlation of the yield with the pressure in the source.

Multiple photon absorption requires a powerful laser beam, and a Nd:YAG laser has, therefore, been used. The fundamental mode is at 1064 nm corresponding to a photon energy of 1.165 eV. The cross section of the laser beam inside the ring was ~2 cm^2 and the pulse energy was typically 0.2 J for second-harmonic, 0.1 J for third-harmonic, and 0.02 J for fourth-harmonic radiation. The absorption cross section depends on the temperature of the molecules and, therefore, does not remain constant in multiphoton absorption, but we can estimate the average number of photons absorbed with the cross section derived from a dielectric model, which has been used for prediction of thermal radiation [7,8]. From Fig. 4 in Ref. [14] we obtain $\sigma[\text{Å}^2]=0.15$, 0.5, and 1.5 for second, third, and fourth harmonic radiation. With the laser-pulse energies and the beam size given above we then obtain the average number of photons absorbed for the three harmonics, $\overline{n}=3.9$, 4.3, and 1.9. These values confirm that our laser intensities should be sufficient for observation of decay after multiphoton excitation.

III. ANALYSIS

The analysis of the data builds upon the description detailed in Ref. [8]. The rate constant for electron emission is given as a function of the internal temperature T by an Arrhenius expression

$$k(T)=\nu \exp(-E_b/k_BT_e), \tag{1}$$

where $E_b=2.67$ eV is the electron binding, k_B is Boltzmann's constant. The excitation energy of the molecule after electron emission is close to $E-E_b$ and the effective emission temperature is the average between the initial and final temperatures, $T_e=T-E_b/2C$. The energy resides in harmonic vibrations, and for $T>1000$ K a good approximation to the internal temperature T is obtained from the excitation energy E through the relation $E[\text{eV}]=7.3+C(T[\text{K}]-1000)$, with the heat capacity $C=0.0138$ eV/K. At 300 K the heat capacity is smaller by a factor of 2.5 and the average excitation energy is 0.52 eV. The caloric curve for C_{60} and the linear fit are illustrated in Ref. [8]. A small correction from the canonical to the microcanonical heat capacity, $C\rightarrow C-k_B$, which was ignored in Ref. [8], has been included here [15].

From consideration of detailed balance in statistical equilibrium between emission and attachment of electrons, one obtains for the pre-exponential factor [2]

$$\nu=\frac{m}{\pi^2\hbar^3}\langle\sigma_a\rangle_{T_f}(k_bT_f)^2\frac{g_f}{g_i}. \tag{2}$$

Here m is the electron mass, and the average of the cross section σ_a for electron attachment contains a weighting by the electron energy and by a Boltzmann factor corresponding to the final temperature T_f. The last factor is the ratio between electron degeneracies in the final and initial states, which for C_{60}^- is equal to 1:3. With an averaged cross section of 60 Å^2 one obtains $\nu=3.0\times10^6(T_f[\text{K}])^2\ \text{s}^{-1}$ [8].

From the detailed studies of emission of thermal radiation from C_{60}^-, we know that the decay rate is modified by photon emission for lifetimes of order 1 ms or longer [6–8]. Owing to the large heat capacity, the radiation can to a good approximation be treated as continuous cooling of the molecule [8]. The radiation intensity is approximately proportional to the sixth power of the temperature, $I_r\simeq AT^6$, and we then obtain an explicit formula for the temperature as a function of time after the excitation,

$$T(t)=T_0(1+5tAT_0^5/C)^{-1/5}, \tag{3}$$

where T_0 is the initial temperature. The yield at time t becomes

$$I(t)=N_0k(T(t))\exp\left[-\int_0^t k(T(t'))dt'\right], \tag{4}$$

where N_0 is a constant and the functions $T(t)$ and $k(T)$ are given by Eqs. (1)–(3).

As illustrated in Fig. 4, we have fitted our measurements using this description. In the optimization we have minimized the sum of squares of the logarithm of the ratio between measurement and fit because the fluctuations are mainly nonstatistical, caused by betatron oscillations as discussed above. Common parameters in the three fits are the attachment cross section and the radiation constant A, and in each fit we have included contributions from two photon numbers. For the measurements with absorption of three fourth-harmonic photons in Fig. 4(a) and four third-harmonic photons in Fig. 4(b), the contribution from absorption of one photon less is very small since the decay rate in Eq. (1) is lower by about two orders of magnitude. This is illustrated by the dot-dashed curves, which show the contribution to the fit from three-photon absorption in Fig. 4(a) and four-photon absorption in Fig. 4(b). We have made a combined fit to the two measurements with the initial energy equal to the thermal energy at room temperature and with a common value of the attachment cross section. This value together with the two normalization constants N_0 for each of the two measurements were varied to optimize the fits, while the cooling parameter A was kept fixed at the value determined by the fit in Fig. 4(c), as discussed below. From the N_0 values, the ratio of the probabilities for three-photon and two-photon absorption is found to be 0.3 in Fig. 4(a), and for Fig. 4(b) the corresponding ratio for absorption of four and three photons is 0.85. We may compare these numbers to the ratios 0.6 and 1.1 in Poisson distributions with the average values of n estimated above, $\overline{n}=1.9$ and $\overline{n}=4.3$. The agreement within a factor of 2 is quite satisfactory in view of the cursory nature of the estimates.

As seen from Eqs. (1) and (2), the decay rate is proportional to the attachment cross section, and this is illustrated by the dotted curves in Fig. 4(a), which include only the contribution from three-photon absorption. The fits in Figs. 4(a) and 4(b) yield an optimum value of $\langle\sigma_a\rangle=42$ Å^2. The main source of error is the uncertainty of the initial thermal energy. A variation of the excitation energy by 0.1 eV gives a 10% variation in the derived cross section. The curvature of the curves stems from radiative cooling. There should also be a contribution from the finite width of the energy distribution since depletion of this distribution from the high-energy side leads to a small positive curvature in a logarithmic plot. This is a very large effect for fullerenes produced at high temperature in an oven [2]. We have made a simulation for a Gauss-

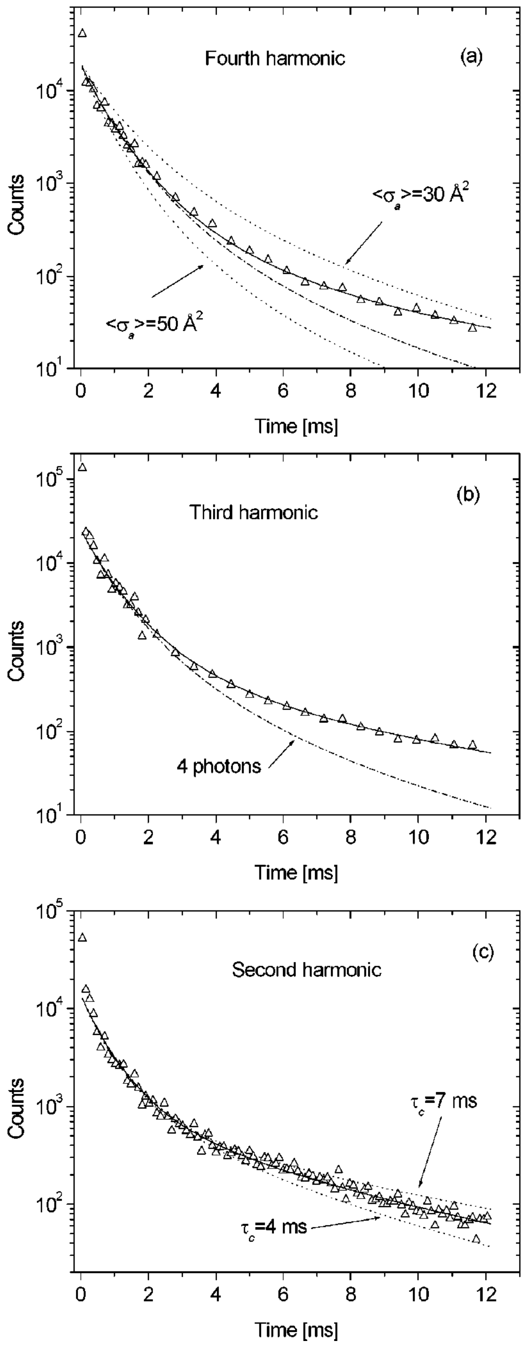

FIG. 4. Analysis of the measurements with (a) fourth-, (b) third-, and (c) second-harmonic radiation from a Nd:YAG laser. The points represent the counts per revolution in spectra of the type illustrated in Fig. 3, and they are plotted against the time t after the laser excitation. In (a) and (b) the counts from five revolutions have been averaged for $t > 2$ ms to reduce fluctuations. The solid lines are fits explained in the text, with attachment cross section $\langle \sigma_a \rangle = 42$ Å^2. The dot-dashed curves in (a) and (b) show the component of the fit corresponding to absorption of three fourth-harmonic photons and four third-harmonic photons, while the dotted curves in (a) illustrate the sensitivity to the value of the cross section. The fits include radiative cooling, with a characteristic cooling time τ_c scaling with T^{-5} and with $\tau_c = 5.5$ ms at $T = 1356$ K, after absorption of five second-harmonic photons. The dotted curves in (c) illustrate the sensitivity of the fit to this parameter.

ian energy distribution with a width corresponding to the rms fluctuations in the canonical distribution at room temperature, $T\sqrt{Ck_B} = 0.2$ eV. The curvature is small compared to that caused by cooling and it has, therefore, been ignored in the analysis.

For the measurement with second-harmonic radiation, the ratio of the probabilities for five- and six-photon absorption is close to unity, and this again agrees within a factor of 2 with the ratio 0.6 obtained from a Poisson distribution with $\overline{n} = 3.9$. The contributions from the two photon numbers are not so well separated, and both the thermal energy and the attachment cross section have, therefore, been fixed in the fit. We have chosen the thermal energy to be slightly higher (0.56 eV) than for the other measurements because the absorption increases strongly with increasing excitation energy in this wavelength region [14,16]. For a Gaussian energy distribution $\propto \exp[-(E - E_0)^2/\beta^2]$ and a probability $\propto \exp(\alpha E)$ for absorption of n photons with energy $\hbar\omega$, the mean energy after absorption is $E_0 + n\hbar\omega + \alpha\beta^2$, and we have estimated the small increase in the thermal energy from this expression.

As can be seen from introduction into Eq. (1) of a first-order expansion of Eq. (3), the radiative cooling may be characterized by a lifetime given by $\tau_c = CT/GI_r$, where the Gspann parameter G equals the magnitude of the exponent in Eq. (1) and is of order $G \sim 24$ [8]. The fit gives $\tau_c = 5.5$ ms at the temperature 1356 K after absorption of five second-harmonic photons, and the dotted curves in Fig. 4(c) illustrate the sensitivity of the fit to a variation of τ_c. The lifetime obtained from Eq. (1) is at this temperature about 16 ms, so the slope in Fig. 4(c) at the longer times is dominated by cooling, with an effective signal-decay time of about 4 ms. From the scaling of τ_c with T^{-5}, the characteristic cooling times after absorption of three third-harmonic and two fourth-harmonic photons are obtained as 8.2 ms and 10.4 ms, and they are one to two orders of magnitude shorter than the decay times given by Eq. (1). As demonstrated by the excellent fits to the tails in Figs. 4(a) and 4(b), the measurements are consistent with this scaling of τ_c, but the fits are not very sensitive to a small variation of the power law. From the cooling time we obtain a value of A corresponding to a radiation intensity of $I_r = 138$ eV/s at 1356 K. This is in good agreement with the value $I_r \simeq 200$ eV/s at 1400 K obtained in Ref. [8] with an analysis including a Planck distribution of photon energies. As noted there, the derived radiation intensity should be about 20% lower with the continuum-cooling description applied here. The value of A is sensitive to the choice of thermal energy for the measurement with second-harmonic radiation: an increase by 0.1 eV leads to an increase of A by about 10%. This gives the dominant contribution to the uncertainty of the result, which we estimate to be 138 ± 20 eV/s at 1356 K, within the continuum-cooling description.

IV. DISCUSSION AND CONCLUSIONS

The method used here, multiple laser excitation of room-temperature clusters, has previously been applied to the study of electron emission from neutral clusters, which are easily produced by a cold source. Good examples are reported in measurements on small Nb clusters [17,18]. Also here the spread in the initial thermal energy was small, and an exponential decay was observed after the laser excitation. However, compared to the time-of-flight measurements in these studies, our measurements of decay in a storage ring cover a much larger range in count rate. This has made it possible to measure simultaneously the decay from two different numbers of absorbed photons and thereby to determine the influence of cooling by photon emission. As discussed in Ref. [2], competition by photon emission may be important also in the experiments on Nb clusters.

According to the ergodic hypothesis, all the available phase space is sampled before the decay. Since the temperatures are moderate in our experiment, $k_BT < 0.2$ eV, the probability for electronic excitation is very small in equilibrium, and all the absorbed energy is transformed into vibrational excitation before the electron by a rare statistical fluctuation receives enough energy to leave the molecule. The applicability of this picture to processes induced by photon absorption has been studied in detail for C_{60}. For photon energies exceeding the ionization energy of 7.6 eV, direct ionization dominates [19], and for multiphoton ionization this domination can extend to somewhat lower photon energies due to the long lifetime of the lowest triplet states in C_{60} (1.7 eV), which are efficiently populated via intersystem crossing [20–25]. Decay of these states could, therefore, be an internal bottleneck for equilibration [26]. This idea has been supported by experiments on ionization after vibrational excitation with infrared photons from a free-electron laser, where a delay of tens of microseconds before onset of electron emission was observed [27]. In this case the bottleneck is approached from the part of phase space without electronic excitation, and simultaneous electronic excitation with a laser was shown to eliminate the delay. It seems quite surprising, however, that the lifetime of the triplet states can remain long at high excitation energies, since triplet lifetimes in aromatic molecules are drastically shortened by excess vibrational energy [21].

For anions, the photon absorption with high probability should result in formation of quartet states, i.e., a spin-1 state in C_{60} combined with the additional electron in the lowest unoccupied molecular orbital to a total spin of 3/2, and such states could also be long lived, at least for not too high excitation energy. However, our results are consistent with a full statistical equilibrium and give no indication of a special role of triplet excitations. Apart from the special problem with long-lived triplet states, the approach to equilibrium should be very fast. For example, experiments with very short laser pulses have indicated that the characteristic time for coupling from electronic to vibrational excitation is ~ 1 ps, only [28].

For electron emission from fullerene anions, it has been unclear whether experiments support an interpretation as emission in statistical equilibrium [1,29,30], but a renewed analysis of the data has indicated that the apparent discrepancies disappear when the width of the energy distributions is taken into account [2]. Our results support this conclusion, and we have determined the effective attachment cross section in the expression for the frequency factor in Eq. (2), $\langle \sigma_a \rangle \simeq 42$ Å^2, with an estimated accuracy of $\pm 20\%$. The result is in reasonable agreement with measured attachment cross sections at low electron energies [3–5] and consistent with the analysis in Ref. [2] of the associated lifetime measurements, which sets upper and lower bounds of 60 Å^2 and 20 Å^2 for the cross section.

The calibration of the frequency factor in the Arrhenius formula in Eq. (1) is valuable for the interpretation of experiments with a broad distribution in excitation energy, which rely on this formula to give a connection between time and temperature [6,8]. Furthermore, the determination of a cooling rate at a well-defined excitation energy has given independent confirmation of the intensity of radiation derived from experiments with fullerene anions injected into ELISA from a hot ion source [8]. The uncertainty of the present results stems mainly from the width of the initial distribution in excitation energy, and it would, therefore, be desirable to be able to cool the Paul trap in the ion source. We are planning a modification of the injection system to include this feature.

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