

Radiatively Self-Cooled Penning-Trapped Electrons: A New Way To Make Gas-Phase Negative Ions from Neutrals of Low Electron Affinity

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Abstract: We present a new method for attachment of self-cooled electrons to gas-phase neutrals of potentially low electron affinity. The cyclotron frequency of electrons in a Penning trap operated at 3 T is sufficiently high that 2 eV electrons injected into the trap from a hot filament cool themselves to room temperature (~ 0.02 eV) in ~ 1 s by classical radiative emission. In fact, we show that radiative cooling can be much more efficient than cooling by electron–neutral or electron–electron collisions. Such cold electrons have high cross-section for attachment to gaseous neutrals of quite low electron affinity (< 0.5 eV). Because both electrons and negative ions can be trapped simultaneously in a Penning trap, the negative ions so formed may be detected by FT-ICR mass spectrometry in the same Penning trap. Compared to conventional chemical ionization, the present method for producing negative ions requires no additional chemical reagent and can be conducted at relatively low pressure by use of pulsed-gas introduction of the sample. The method is demonstrated by successful electron attachment to polycyclic aromatic hydrocarbons with electron affinities as low as 0.49 eV (anthracene) and 0.45 eV (pyrene).

Introduction

Electron impact ionization mass spectrometry (EI-MS) remains the most popular method for the detection and identification of volatile environmental chemicals. EI-MS produces molecular and fragment ions, typically by 70 eV electron bombardment of gas-phase organic neutral molecules.¹ The main disadvantage of EI is extensive molecular fragmentation, which reduces the molecular ion abundance and makes it difficult to distinguish primary and fragment ions in complex mixtures.

Although EI usually produces mainly positive (generally radical) ions, capture of low-energy electrons by neutrals produces negative ions. This so-called “electron capture” mass spectrometry (EC-MS) can be outstandingly selective and sensitive for detection of species with high electron affinity (e.g., polycyclic aromatic hydrocarbons), and is commonly used to identify and quantitate very small amounts of selected environmental contaminants.¹ Conventionally, low-energy electrons for EC-MS are produced by “negative ion chemical ionization” (NCI). In the NCI technique, a buffer gas such as methane at ~ 1 Torr is bombarded by high-energy electrons (> 70 eV) to generate low-energy secondary electrons. Those secondary electrons are cooled to room temperature by collisions with buffer gas (hence the need for high pressure). Resonant electron capture to produce a molecular negative ion has maximal reaction cross section at near-zero electron energy.



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Buchanan² has successfully used NCI to generate the negative ions for mass analysis by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Because FT-ICR MS operates optimally at $\leq 10^{-8}$ Torr, Buchanan used either a steady low pressure (10^{-6} to 10^{-4} Torr) or a higher pulsed pressure (up to a few tenths of a torr) of methane reagent gas to achieve the same number of electron–methane collisions as in conventional NCI.

Here we demonstrate a new method to produce very-low-energy electrons to form negative ions by electron attachment in a Penning (ICR) ion trap. The method consists simply of trapping pulsed electrons of ~ 2 eV emitted from a filament and then allowing the electrons to cool themselves quickly (~ 1 s) to room temperature by cyclotron radiation in a 3.0 T magnetic field. The cold-trapped electrons then attach readily to neutral molecules admitted to the trap from a heated solids probe via a pulsed valve. Advantages of the method are described.

Experimental Section

The present experiments were conducted with a Finnigan FTMS-2000 instrument (Finnigan FTMS, Madison, WI) equipped with 1.875-in. dual cubic traps (Figure 1), an Odyssey data system, and a 3-T superconducting magnet. A pulse of electrons was generated by a voltage gate in front of a filament outside the cryostat. Figure 2 shows the experimental event sequence. Electrons were confined and cooled in the source compartment of the dual trap as follows. The source end cap electrode is maintained (except for the quench event) at -9 V throughout the event sequence. We begin by simultaneously opening the electron gun gate (with the analyzer trap end cap electrode and conductance limit electrodes at 0 V to allow electrons to pass through them). The electron gun gate is opened for 1.1 ms and the conductance limit trap plate is left at 0 V for 1 ms. The electron gun gate thus extends 0.1 ms (i.e. ~ 1000 electron axial oscillation cycles—see below)

(2) Buchanan, M. V.; Rubín, I. B.; Wise, M. B.; Glish, G. L. *Biomed. Environ. Mass Spectrom.* **1987**, *14*, 395–399.

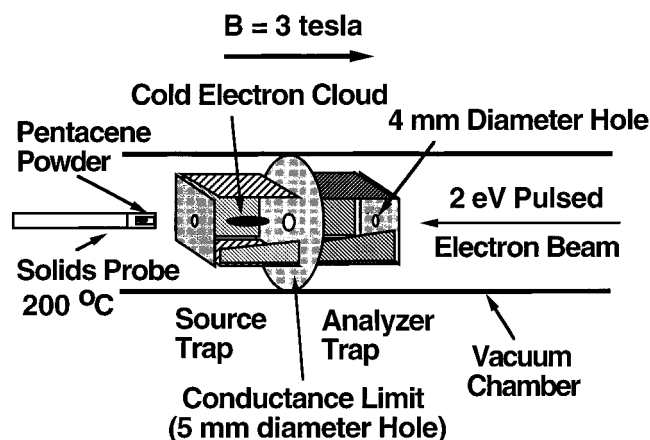


Figure 1. Schematic diagram of a dual cubic Penning trap for production of self-cooled trapped electrons for attachment to gas-phase neutrals formed by evaporation from a heated solids probe.

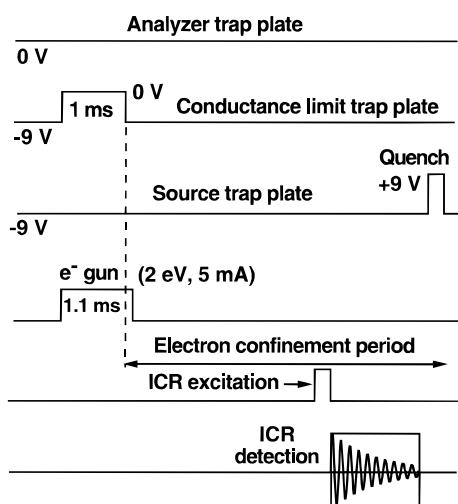


Figure 2. Experimental event sequence (see text).

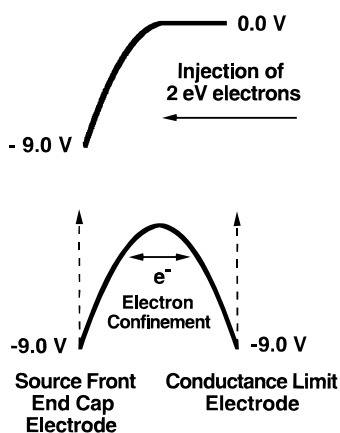


Figure 3. Electrostatic potential along the magnetic field (axial) direction in the source Penning trap: (top) during electron injection; (bottom) during electron confinement period. Electrons are trapped by lowering the conductance limit (negative) potential magnitude to admit electrons (top) and then raising the (negative) potential magnitude on the conductance limit to confine electrons for subsequent cooling and attachment to neutrals.

beyond the instant at which the conductance limit electrode is changed to -9 V. In this way, we ensure the capture of the pulsed electrons in the source compartment. The mechanism for electron trapping is shown in Figure 3. We reduce the conductance limit trap plate voltage to 0 V to allow electrons to enter the trap. After the electrons are reflected

at the conductance limit electrode, we lower its voltage to -9 V, thereby trapping electrons with less than 9 eV of translational energy.

Theory: Radiative Cooling of Electrons Trapped in a Magnetic Field

Charged particles (whether positive ions, negative ions, or electrons) exhibit three natural motions in a Penning trap (i.e., a region of constant spatially homogeneous magnetic field and axial (along the magnetic field direction) quadrupolar electrostatic potential):³ cyclotron rotation at frequency ω_+ , magnetron rotation at frequency ω_- , and axial linear oscillation at frequency ω_z .

$$\omega_{\pm} = \frac{\omega_c}{2} \pm \sqrt{\frac{\omega_c^2}{4} - \frac{\omega_z^2}{2}} \quad (1)$$

$$\omega_z = \sqrt{\frac{2\alpha q V_T}{ma^2}} \quad (2)$$

in which

$$\omega_c = \frac{qB}{m} \quad (3)$$

is the ion cyclotron frequency, α is a trap geometric factor (2.77373 for a cubic trap), q and m are ion charge and mass, V_T is the voltage applied to each end cap electrode, and a is the length of one side of the cube. For electrons at $B = 3$ T, $a = 4.60$ cm and $V_T = 9$ V,

$$\frac{\omega_+}{2\pi} = 84 \text{ GHz}, \quad \frac{\omega_-}{2\pi} = 0.72 \text{ kHz}, \quad \frac{\omega_z}{2\pi} = 11 \text{ MHz}, \quad \frac{\omega_c}{2\pi} = 84 \text{ GHz} \quad (4)$$

Radiative Damping. However, by Maxwell's laws, an accelerating charge radiates electromagnetic waves, thereby continuously losing (kinetic) energy.⁴ It is well-known that this radiation damps the charged particle's motion.⁵ Because the transition probability for such electric dipole radiation is proportional to the square of the oscillation or rotation frequency of the charge, appreciable radiative decay occurs only for high-frequency motions.³ Thus, for protons or heavier ions in FT-ICR, the (cyclotron) motional frequencies fall in the radio frequency range, and radiative decay is negligibly slow (e.g., 5.9×10^7 year time constant for singly-charged ions of 100 u at 3 T). Radiative decay is also negligible for electron magnetron motion, and is slow even for electron axial oscillation (e.g., 266-day time constant at -9 V trapping potential in a 1.875-in. cubic trap). However, electron cyclotron rotation in a strong magnetic field is so fast that radiative decay is the dominant energy relaxation mechanism at low neutral pressure ($\leq 10^{-8}$ Torr).

Following Feynman's treatment of the theory of radiation damping,⁶ Comisarow⁷ obtained a radiation damping time

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(7) Comisarow, M. B. *Ion Cyclotron Resonance Spectrometry II*; Hartmann, H., Wanczek, K.-P., Eds.; Springer-Verlag: Berlin, 1982; pp 484–513.

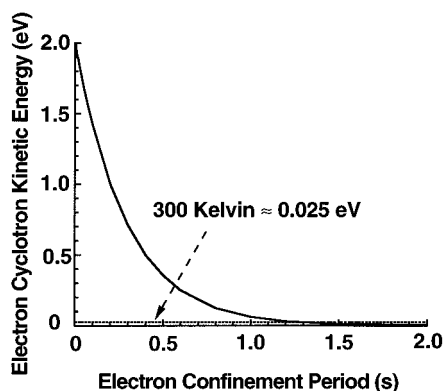


Figure 4. Electron cyclotron kinetic energy vs time during the period of electron confinement in the source trap. Note that electrons self-cool in ~ 1 s at 3 T by radiative emission.

constant of 1.4 million years for singly charged Penning-trapped ions of 100 u at 1 T, demonstrating that radiation damping of molecular ions in ICR is negligible as a relaxation mechanism. However, cooling of electrons by radiative damping in ICR was not considered by Comisarow.

Brown and Gabrielse³ evaluated the radiative damping constant for ions in a Penning trap:

$$\frac{dE}{dt} = -\gamma_c E \quad (5)$$

$$E(t) = E_0 \exp(-\gamma_c t) \quad (6)$$

$$\gamma_c = \frac{4e^2\omega_+^2}{3m_e c^3} \frac{\omega_+}{\omega_+ - \omega_-} \approx \frac{4e^2\omega_c^2}{3m_e c^3} \quad (7)$$

in which E , r , e , and m_e are the cyclotron energy, cyclotron radius, elementary charge, and electron mass. For electrons in a 3-T magnetic field we have

$$\gamma_c^{-1} = 0.29 \text{ s} \quad (8)$$

The experimental value of γ^{-1} for the cooling time constant is a few times longer than the value calculated from eq 8, because the Penning trap electrodes do not provide an ideal microwave cavity for electron cyclotron radiation.³

The initial energy of trapped electrons in the present experiments is about 2 eV. During the radiative cooling process, the electron cyclotron energy as a function of time is shown in Figure 4. Because of imperfectly quadrupolar trapping potential, the cyclotron motion will couple with the axial motion.^{8,9} Thus, radiative cooling of electron cyclotron motion will also cool the electron axial motion, and the electrons should quickly cool to room temperature in about 1 s.

Collisional Damping. Note that collisions between the electrons and the buffer gas ($\sim 4 \times 10^{-8}$ Torr) in the Penning trap do not cool the electrons efficiently. As a rough estimate, the rate constant for collisions between electrons and background gas at 4×10^{-8} Torr is given by

$$\gamma_{\text{collision}} = n\sigma v = (1.3 \times 10^9 \text{ cm}^{-3})(10^{-16} \text{ cm}^2) \times (2 \times 10^7 \text{ cm s}^{-1}) \approx 2.6 \text{ s}^{-1} \quad (9)$$

in which n is the density of buffer gas, σ is the hard sphere

collision cross section between electron and background gas, and v is the velocity of a 1 eV electron relative to the background gas. However, the efficiency of energy transfer from an electron to the background gas is very low because of the very small electron mass. The energy loss per electron for each collision is¹⁰

$$\Delta E = 4 \frac{m_e}{m_e + m_b} \frac{m_b}{m_e + m_b} E_e = 2 \times 10^{-5} \text{ (eV)} \quad (10)$$

in which m_b is the mass of the background gas and E_e is the energy of the electron. Therefore the collision-induced electron energy loss rate constant is

$$\Delta E \gamma_{\text{collision}} = 5.2 \times 10^{-5} \text{ (eV s}^{-1}\text{)} \quad (11)$$

This energy loss is thus negligible compared to that from radiative cooling (eqs 5, 8, $E_e = 1$ eV):

$$\left(\frac{dE_e}{dt}\right)_{\text{radiation}} = -\gamma_c E_e = -3.45 \text{ (eV s}^{-1}\text{)} \quad (12)$$

Resistive Damping. Note that resistive damping cannot cool electrons efficiently in the present experiments. Because we did not introduce an inductor to produce a resonant LCR circuit to damp electron cyclotron motion,³ we have simply an RC circuit. Comisarow^{7,11} has discussed the resistive damping of ion cyclotron motion by an RC circuit. R is the preamplifier input resistance, which is about 1 M Ω ; the capacitance, C , is about 30 pF in our case.¹² When $R \ll 1/(\omega_c C)$, the time constant, τ_R , for resistive damping of coherent ion cyclotron motion is^{7,11}

$$\tau_R = \frac{2m_e d^2}{Nq^2 R} \text{ (mks)} \quad (13a)$$

When $R \gg 1/(\omega_c C)$, τ_R becomes^{7,11}

$$\tau_R = \frac{2RB^2 C^2 d^2}{Nm_e} \text{ (mks)} \quad (13b)$$

in which N is the number of coherently orbiting electrons, m_e is the electron mass, B is magnetic field, R and C are the circuit equivalent resistance and capacitance, and d is the distance between two ICR detection plates.

Here, $R = 10^6 \Omega \gg 1/(\omega_c C) = 1/(2\pi \times (85 \times 10^9) \times (30 \times 10^{-12})) = 0.06 \Omega$, and we may use eq 13b to estimate the resistive damping time constant for electron coherent cyclotron motion.

For $R = 10^6 \Omega$, $C = 30$ pF, $B = 3$ T, $d = 0.05$ m, $N = 10^6$, and $m_e = 9.1 \times 10^{-31}$ kg, eq 13b yields

$$\tau_R = \frac{2RB^2 C^2 d^2}{Nm_e} = 4.5 \times 10^7 \text{ s} \approx 17 \text{ months}$$

Damping will of course be much slower if (as in the present case) electron cyclotron motion is not coherent. Therefore,

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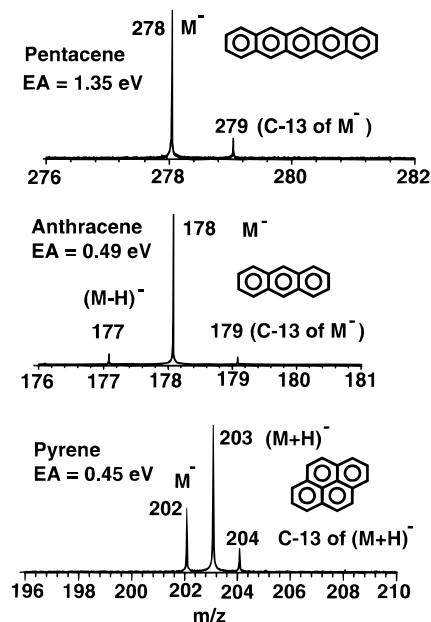
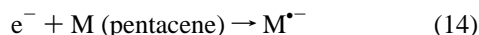


Figure 5. Negative ion FT-ICR mass spectra of pentacene, anthracene, and pyrene formed in a cubic Penning trap by attachment of trapped self-cooled electrons.

resistive damping cannot cool electrons efficiently in the present experiments.

Results: Attachment of Cold-Trapped Electrons to Pentacene, Anthracene, and Pyrene

Pentacene. Reaction of cold-trapped electrons with gas-phase pentacene yields only $M^{\bullet-}$ ions, as seen in Figure 5.



$$\frac{dN_{M^{\bullet-}}}{dt} = k_a N_e \quad (15)$$

$$N_e + N_{M^{\bullet-}} = N_0 \quad (16)$$

in which N_e and $N_{M^{\bullet-}}$ are the numbers of electrons and negative pentacene ions. N_0 is the initial number of trapped and cooled electrons.

$$k_a = n_M \sigma v \quad (17)$$

k_a is the electron attachment rate constant (s^{-1}), n_M is the number density of pentacene molecules, and σ (cm^2) and v ($cm s^{-1}$) are the electron attachment cross section and electron velocity relative to a pentacene molecule. Combining eqs 15 and 16 and taking k_a as constant with time, we obtain

$$N_{M^{\bullet-}} = N_0(1 - \exp(-k_a t)) \quad (18)$$

A plot of trapped negative pentacene molecular ion relative abundance as a function of electron confinement period is shown in Figure 6. Fitting that data to eq 18, we obtain the rate constant for electron attachment to pentacene:

$$k_a = 11.9 \pm 1.7 s^{-1} \quad (19)$$

With an unheated sample probe, the background pressure is $\sim 1 \times 10^{-8}$ Torr. To generate gas-phase pentacene molecules, we heated pentacene powder in the solids probe (just outside the ICR source side trap) to 200 °C. The pressure from an ion

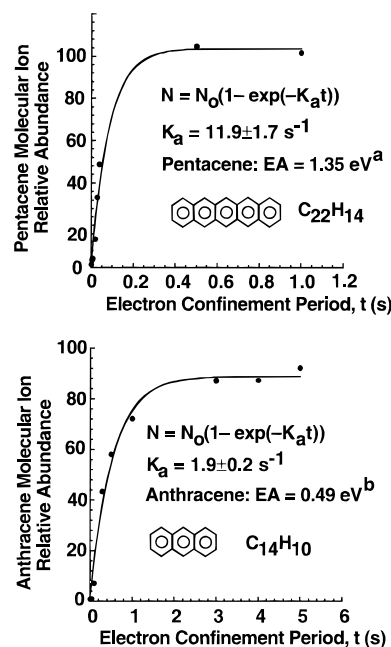


Figure 6. Relative FT-ICR abundances of pentacene (top) and anthracene (bottom) molecular negative ions as a function of duration of exposure to trapped self-cooled electrons. Rate constants are obtained by fitting the experimental curves to eq 18 (see text): a, ref 14; b, ref 22.

gauge ~ 1 m from the ICR ion trap was 6×10^{-8} torr. Given the different ionization gauge sensitivity for different gases,¹³ the true pressure at the gauge is somewhat lower. However, the pressure at the ion trap will be higher than that at the (remote) ion gauge. We therefore simply use the raw ion gauge reading as an estimate of the neutral pressure in the trap to obtain an estimated pentacene number density,

$$n_M = 1.9 \times 10^9 cm^{-3} \quad (20)$$

Combining eqs 17, 19, and 20, we obtain an approximate collision rate constant

$$\sigma v = 6.2 \times 10^{-9} cm^3 s^{-1} \quad (21)$$

This value is somewhat larger than the literature value ($1.59 \times 10^{-9} cm^3 s^{-1}$) from Crocker *et al.*,¹⁴ possibly due to our approximate pressure estimate for neutral pentacene vapor. Finally, to test for possible effects of residual trapped room temperature electrons, we lowered the trapping potential to 0 V for 0, 30, 35, and 50 μs (see Figure 7); because the FT-ICR mass spectral resolving power is nearly unaffected, we infer that essentially all of the trapped electrons have attached to neutral pentacene molecules.

Anthracene. Reaction of cold-trapped electrons with anthracene yields $M^{\bullet-}$ along with a minor ($\sim 8\%$) $(M-H)^{\bullet-}$ component (see Figure 5). The experiment was conducted as for pentacene. Anthracene powder was heated to 100 °C, to yield an ion gauge pressure of $\sim 2 \times 10^{-7}$ Torr. At this approximate pressure, the anthracene number density is

$$n_M = 6.6 \times 10^9 cm^{-3} \quad (22)$$

The relative abundance of anthracene negative ions as a function of electron confinement period is shown in Figure 6. Fitting

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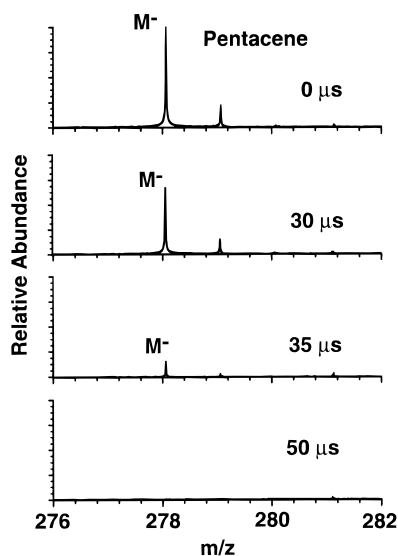


Figure 7. FT-ICR mass spectra of negative ions formed by self-cooled electron attachment to pentacene, after residual trapped electrons are allowed to escape by lowering the end cap potential to 0 V for 0, 30, 35, and 50 μs . Although some molecular negative ions also escape, the line shape is relatively unaffected, showing that the effect of residual trapped electrons is negligible.

the data in Figure 6 to eq 18 yields the electron attachment rate constant

$$k_a = 1.9 \pm 0.2 \text{ s}^{-1} \quad (23)$$

and collision rate constant (from eq 22)

$$\sigma v = 0.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \quad (24)$$

for anthracene.

Pyrene. Reaction of cold-trapped electrons with pyrene yields both $\text{M}^{\bullet-}$ and $(\text{M} + \text{H})^-$ ions (see Figure 5). Pyrene powder was heated to 100 $^\circ\text{C}$ to yield an ion gauge pressure of $\sim 2 \times 10^{-7}$ Torr. The pyrene number density at that pressure is

$$n_M = 6.6 \times 10^9 \text{ cm}^{-3} \quad (25)$$

Figure 8 shows that the abundance of $\text{M}^{\bullet-}$ increases and then decreases, whereas $(\text{M} + \text{H})^-$ increases monotonically with increasing electron confinement period. The sum of the $\text{M}^{\bullet-}$ and $(\text{M} + \text{H})^-$ ion abundances (also shown in Figure 8) can be fitted to

$$N_{\text{M}^{\bullet-}} + N_{(\text{M}+\text{H})^-} = N_0(1 - \exp(-k_a t)) \quad (26)$$

to obtain a combined rate for electron attachment to M and MH.

$$k_a = 0.67 \pm 0.09 \text{ s}^{-1} \quad (27)$$

Combining eqs 25 and 27 yields a collision rate constant for attachment of cold electrons to pyrene.

$$\sigma v = 0.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \quad (28)$$

The results for cold electron attachment to pentacene, anthracene, and pyrene are summarized in Table 1.

For pyrene we also observed a major $(\text{M} + \text{H})^-$ signal (see Figure 5). Consistent with that result, Iida and Daishima¹⁵ previously found $(\text{M} + \text{H})^-$ ions with high abundance in mass

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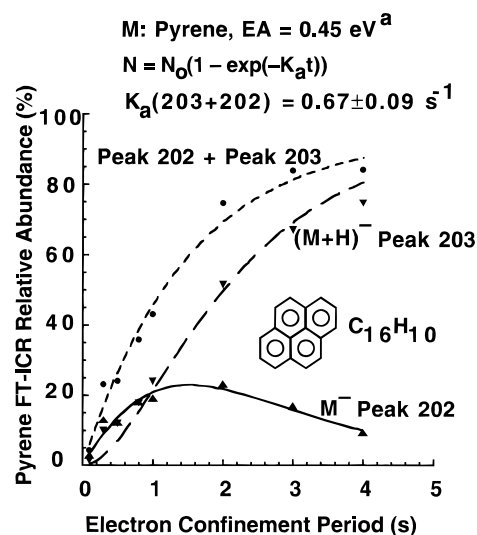


Figure 8. FT-ICR peak abundance of negative ions formed from pyrene, as a function of duration of exposure to trapped self-cooled electrons. The electron attachment rate is calculated by fitting the sum of the relative abundances of $\text{M}^{\bullet-}$ (m/z 202) and $(\text{M} + \text{H})^-$ (m/z 203) to eq 18 (see text): a, ref 22.

Table 1. Rate Constants for Attachment of Self-Cooled Trapped Electrons to Pentacene, Anthracene, and Pyrene in a Penning (ICR) Ion Trap at 3.0 T

	pentacene	anthracene	pyrene
mass (u)	278	178	202
electron affinity (eV)	1.35 ¹⁴	0.49 ²²	0.45 ²²
attachment rate constant (s^{-1})	11.9 ± 1.7	1.9 ± 0.2	0.7 ± 0.1
approximate pressure (Torr)	6×10^{-8}	2×10^{-7}	2×10^{-7}
rate constant ($\text{cm}^3 \text{ s}^{-1}$)	6.2×10^{-9}	0.3×10^{-9}	0.1×10^{-9}

spectra of some PAHs (such as anthracene, pyrene, benz[a]-anthracene). McEwen and Rudat¹⁶ also observed $(\text{M} + \text{H})^-$ ions for the case of 7,7,8,8-tetracyanoquinodimethane. Although Low *et al.*¹⁷ have shown that formation of $(\text{M} + \text{H})^-$ ions is favored for large-ring PAH compounds (>4 rings), we did not observe $(\text{M} + \text{H})^-$ ions for pentacene. Low *et al.*¹⁷ attributed $(\text{M} + \text{H})^-$ either to a fast radical reaction between H and $\text{M}^{\bullet-}$ or a hydride transfer of an H^- anion to the neutral PAH molecule. Here, a fast radical reaction between H and $\text{M}^{\bullet-}$ appears likely because the $\text{M}^{\bullet-}$ signal decreases with an increase in $(\text{M} + \text{H})^-$.

Discussion

The main advantages for our new method for producing low-energy electrons are nearly the same as those of Larmee *et al.*,¹⁸ who used an electron monochromator to replace a standard (NICI) source for analysis of organophosphate pesticides: we do not need a reagent gas, and the pressure in the FT-ICR cell can be as low as 10^{-9} Torr for high-resolution mass analysis; there is no chemical ionization plasma; and electron attachment is facilitated by the low electron energy (~ 0.02 eV). Moreover, the use of reagent gas can result in ion–molecule reactions which complicate the interpretation of the mass spectra;¹⁹ cold electron attachment avoids that problem. The cold electrons in our Penning trap can also cool the negative ions by

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sympathetic cooling.²⁰ Finally, negative ions are formed only near the center of the Penning trap because that is where the cold electrons are, thereby producing a compact ion packet for optimal FT-ICR mass resolving power and sensitivity.

For example, Buchanan was unable to generate anthracene and pyrene negative ions in FT-ICR by the standard NICI method, because their electron affinities are too small:² the electron affinities for both anthracene and pyrene are less than 0.5 eV. However, we are able to generate (and detect by FT-ICR) both anthracene and pyrene negative ions by attachment of self-cooled electrons.

In an alternative recent experimental approach to attachment of low-energy electrons to neutrals in the presence of nitrogen buffer gas at atmospheric pressure, Liu *et al.* coupled an ion mobility spectrometer *via* a supersonic molecular beam to a quadrupole mass spectrometer.²¹ Although their technique allows for quantitation of electron attachment kinetics, it requires entrainment of the desired neutrals in a supersonic molecular beam.

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Conclusion

As a new method for generating negative ions, we produce a pulse (~1 ms) of electrons of ~2 eV kinetic energy from a hot filament electron gun. We admit electrons into a Penning ion trap by lowering the end cap trapping voltage. Once the electrons are inside, the trapping voltage is raised to confine (for a minute or more) electrons of energy less than the trapping potential. In the key step, the trapped electrons self-cool in a magnetic field of 3 T to near room temperature by cyclotron radiative emission in about 1 s. In this way, we are able to generate, trap, and cool ~10⁶ electrons at 10⁻⁸ T background pressure. Those cold electrons will then attach to neutrals of electron affinity as low as 0.45 eV to form abundant molecular negative ions from pentacene, anthracene, and pyrene. The method operates without the need for high pressure or plasma conditions, and should be generally useful as a new way of making and trapping negative ions for ion–molecule chemistry observed by FT-ICR mass analysis.

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