

# Vibrational cooling in a cold ion trap: Vibrationally resolved photoelectron spectroscopy of cold $C_{60}^-$ anions

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We demonstrate vibrational cooling of anions via collisions with a background gas in an ion trap attached to a cryogenically controlled cold head (10–400 K). Photoelectron spectra of vibrationally cold  $C_{60}^-$  anions, produced by electrospray ionization and cooled in the cold ion trap, have been obtained. Relative to spectra taken at room temperature, vibrational hot bands are completely eliminated, yielding well-resolved vibrational structures and a more accurate electron affinity for neutral  $C_{60}$ . The electron affinity of  $C_{60}$  is measured to be  $2.683 \pm 0.008$  eV. The cold spectra reveal complicated vibrational structures for the transition to the  $C_{60}$  ground state due to the Jahn-Teller effect in the ground state of  $C_{60}^-$ . Vibrational excitations in the two  $A_g$  modes and eight  $H_g$  modes are observed, providing ideal data to assess the vibronic couplings in  $C_{60}^-$ . © 2005 American Institute of Physics. [DOI: 10.1063/1.1998787]

Temperature is a critical issue in gas phase spectroscopy and chemistry. Many techniques, such as adiabatic expansion,<sup>1,2</sup> evaporative cooling,<sup>3,4</sup> laser cooling,<sup>5,6</sup> and sympathetic cooling,<sup>7</sup> have been developed to trap and cool atomic ions and electrons. It has been demonstrated that atomic ions can be cooled down to microkelvin or even nanokelvin. However, cooling molecular ions and clusters, both translationally and internally, still remains a formidable challenge.<sup>8</sup> Very often “cooling ions” in the mass spectrometry community really means collisional damping and reducing ion temperatures down to or below room temperature.<sup>9</sup> While this is satisfactory in most cases in mass spectrometry applications, it is far less ideal for spectroscopy studies and ion molecule reactions. At room temperature, molecular species can contain substantial internal energies. As a result, thermodynamical properties of ions cannot be determined accurately, and their spectra are often broadened. In addition, many unique and novel conformations and weakly bound molecular species only exist at low temperatures. Therefore, cooling and controlling temperatures of molecules way below room temperature is critical in chemical reaction dynamics and molecular spectroscopy. The supersonic expansion<sup>10</sup> and helium nanodroplet matrix<sup>11–14</sup> are two powerful and effective ways to cool neutral molecules. For cooling molecular ions, extra efforts are needed due to the high temperatures usually accompanying the ion formation processes. Thermalization in a liquid- $N_2$ -cooled environment plus supersonic expansion has been used to achieve subroom temperature cooling effect in ion-beam experiments.<sup>15</sup> One elegant example of producing extremely cold-solvated cluster ions has been demonstrated by Robertson *et al.* using the so-called argon tagging and evaporative cooling technique.<sup>16</sup>

Collisions of ions with a buffer gas commonly serve to cool atomic and molecular ions in the mass spectrometry community.<sup>9,17</sup> Gerlich and co-workers have extended this method to produce extremely cold molecular ions in a 22-pole radio-frequency ion trap attached to a cryogenic cold head.<sup>18</sup> Parks and co-workers have demonstrated the collisional cooling of cluster ions,  $C_{60}^+$  in particular, in a temperature-controlled Paul trap attached to a liquid- $N_2$ -cold plate.<sup>19</sup> The basic principle of these techniques is that a buffer gas used as a thermal bath fills the entire ion trap volume at a well-defined temperature and pressure in the ion storage device. Ions in the storage cell are confined kinetically by a time-varying electric field and thermalize both internally and translationally with the buffer gas by collisions.

In this communication, we report a variable temperature photoelectron spectroscopy (PES) apparatus utilizing collisional cooling of anions in a Paul trap, which is attached to a cryogenically controlled cold head (10–400 K). We demonstrate that we can effectively cool the  $C_{60}^-$  anion and completely eliminate hot band transitions in its PES spectra. The relatively large size of  $C_{60}^-$  serves as an ideal test case for the cooling effect in our apparatus.

One of the challenges in studying  $C_{60}$  in the gas phase is to generate sufficiently cold  $C_{60}$  ions since it contains a huge amount of internal energy even at room temperature ( $\sim 1$  eV) due to its large number of internal degrees of freedom.<sup>20</sup> For example, despite substantial experimental efforts, all previous experiments on  $C_{60}^-$  were plagued by significant thermal effects.<sup>21–23</sup> In 1999, we reported a vibrationally resolved photoelectron spectrum of  $C_{60}^-$  produced from an electrospray ionization (ESI) source and using a room-temperature ion trap.<sup>24</sup> Although vibrational structures were resolved, significant hot band transitions were present. Despite the high symmetry of neutral  $C_{60}$ , the vibrational

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structures observed in the PES spectra of  $C_{60}^-$  were very complicated due to the vibronic coupling in the ground state of the anion. The vibronic coupling in  $C_{60}^-$  is related to the electron-phonon coupling important for the superconductivity of the alkali-doped fullerenes.<sup>25–28</sup> The vibrational structures in the PES spectrum of  $C_{60}^-$  have been used to deduce the electron-phonon coupling constants based on a spectrum that contains significant thermal broadening.<sup>23</sup> More accurate electron-phonon coupling constants would require a vibrationally cold spectrum.

Our new low-temperature PES apparatus consists of an ESI source, a cryogenically cooled ion trap, and a magnetic-bottle time-of-flight photoelectron analyzer.<sup>29</sup> The ESI source and the magnetic-bottle photoelectron spectrometer are similar to that described previously.<sup>30</sup> The preparation of the  $C_{60}$  solution was according to literature procedures used to generate  $C_{60}^-$  anions in an acetonitrile solution,<sup>31</sup> which was used in the electrospray directly. The anions produced from the ESI source are guided by a rf-only octopole and transported via a quadrupole mass filter (operated in the rf-only mode) into a three-dimensional (3D) Paul trap. The trap is attached to the cold head of a cryostat, which consists of a closed-cycle helium refrigerator and a feedback heating system. Temperatures of the trap can be controlled from 10 to 400 K. Ions are stored and accumulated for a period of 20–100 ms and are cooled via translational and rovibrational energy transfers to a background gas for  $\sim 2000$ – $10\,000$  collisions ( $\sim 1$ -mTorr  $N_2$  temperatures above 70 K or 1-mTorr 20%  $H_2$  in helium for temperatures below 70 K). The trap is operated at low  $q$  values ( $<0.3$ ) to avoid possible rf heating.<sup>32</sup> The cooled ions are pulsed out of the trap at a 10-Hz repetition rate and are separated in a linear time-of-flight (TOF) mass spectrometer.

The ions of interest are mass gated and decelerated before being intercepted by a detachment laser beam in the interaction zone of the magnetic-bottle electron analyzer. In the current experiment, three detachment photon energies are used: 355 nm (3.496 eV) and 266 nm (4.661 eV) from a Nd:yttrium aluminum garnet (YAG) laser, and 193 nm (6.424 eV) from an ArF excimer laser. The detachment laser is operated at 20 Hz with the ion-beam off on alternate shots for background subtraction. The photodetached electrons are collected with nearly 100% efficiency by the magnetic-bottle and analyzed in a 5-m-long electron flight tube. The electron energy resolution of the apparatus is  $\Delta E/E \sim 2\%$ , i.e., 20 meV for 1 eV electrons. Photoelectron time-of-flight spectra are collected and then converted to kinetic-energy spectra, calibrated by the known spectra of  $ClO_2^-$  (Ref. 33) and  $I^-$ . The electron binding-energy spectra presented here are obtained by subtracting the kinetic-energy spectra from the detachment photon energies.

Figure 1 shows the 355-nm photoelectron spectra of  $C_{60}^-$  at two different trap temperatures, 300 K (dot line) and 70 K (solid line). We have also taken the spectrum at 18-K ion trap temperature, but did not observe any changes relative to the spectrum taken at the 70-K trap temperature. The spectra in Fig. 1 represent the transition from the ground state of  $C_{60}^-$  to that of neutral  $C_{60}$  with significant vibrational excitations. The room-temperature spectrum, which is similar to that re-

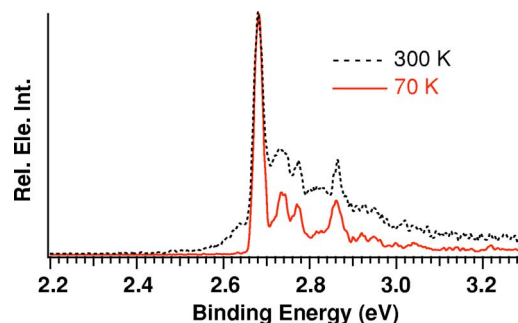


FIG. 1. Comparison of the 355-nm photoelectron spectra of  $C_{60}^-$  taken at 300-K (dotted) and 70-K (solid) ion trap temperatures. Note the disappearance of vibrational hot bands at the low binding-energy side in the low-temperature spectrum.

ported previously,<sup>24</sup> exhibits a significant low-energy tail extending to about 2.4 eV due to the vibrational hot bands in  $C_{60}^-$ . At the 70-K trapping temperature, the vibrational hot bands are almost completely eliminated. Only a few electron counts were observed in the hot band region. We estimated that the vibrational temperature of the  $C_{60}^-$  anions were less than 90 K, at which the population of vibrational hot bands in  $C_{60}^-$  was negligible. The 70-K spectrum, taken at otherwise identical conditions, is also significantly better resolved. The 0-0 transition at 2.683 eV, which defines the electron affinity of  $C_{60}$ , has a line width [full width at half maximum (FWHM)] of 20 meV, characteristic of our instrumental resolution at that energy. In particular, the relative intensities of the vibrational excited states are all reduced in the cold spectrum due to the elimination of hot bands. Since the relative intensities of the vibrational excited states in the photoelectron spectrum were used to evaluate the electron-phonon coupling constants in fullerenes,<sup>23</sup> the current cold spectrum should provide the ideal data set to assess the electron-phonon coupling.

The full set of cold  $C_{60}^-$  spectra at all three photon energies is shown in Fig. 2. Both the 266- and 193-nm spectra are also better resolved compared to the room-temperature spectra (not shown). The vibrational structures in the ground-

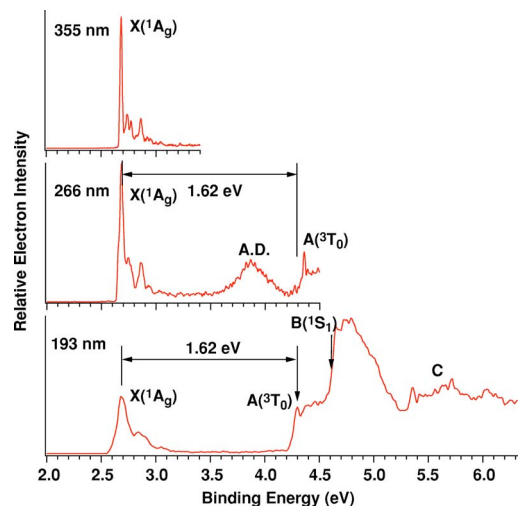


FIG. 2. Photoelectron spectra of cold  $C_{60}^-$  at 355, 266, and 193 nm. All spectra were taken at an ion trap temperature of 70 K.

state transition are well resolved in the 266-nm spectrum. It appears that sharp vibrational features are also resolved for the first excited state ( ${}^3T_0$ ) of  $C_{60}$  in the 266-nm spectrum. The vibrationally resolved features allow an accurate measurement of the excitation energies for the lowest triplet state of  $C_{60}$  ( $1.62 \pm 0.01$  eV), which is optically forbidden. Our previously reported value of 1.57 eV was underestimated due to the thermal broadening in the A band.<sup>24</sup> The broadband, centered around 3.9 eV in the 266-nm spectrum and absent in the 193-nm spectrum, is due to autodetachment, as discussed previously.<sup>24</sup> At 193 nm, the high binding-energy part of the spectrum is continuous even under the cold experimental conditions due to the high density of electronic states.

In  $C_{60}^-$  the extra electron occupies the lowest triply degenerate  $t_{1u}$  orbital, giving rise to a  ${}^2T_{1u}$  state. The degenerate electronic state of  $C_{60}^-$  is Jahn-Teller unstable and is the cause for the extensive vibrational excitation in the photodetachment transition.<sup>23,24</sup> From the position of the 0-0 peak, we measured the electron affinity of  $C_{60}$  to be  $2.683 \pm 0.008$  eV, consistent with our previous electron affinity (EA) value determined from the room-temperature spectrum ( $2.689 \pm 0.008$  eV).<sup>24</sup> The current measurement at low temperature should be more accurate, although the experimental uncertainty remains the same. Our electron affinity obtained using vibrationally cold  $C_{60}^-$  in the current experiment is significantly higher than the  $2.666 \pm 0.001$ -eV value reported previously in a threshold photodetachment experiment in an ion storage ring.<sup>22</sup> The 2.666-eV value was obtained by fitting the detachment threshold using Wigner's threshold law. In principle, this method should yield much more accurate electron affinities for anions. The reasons for this discrepancy are unclear at present, but might be related to the following two potential problems in the previous experiment,<sup>22</sup> which would lead to the low value. First, the signal-to-noise ratio is very poor near the threshold, making it difficult to be fitted with the threshold law. Second, the ions in the storage ring are cooled radiatively and are assumed to be cold. But in reality, the ion temperature is not known. Any hot band transition would lead to a lower detachment threshold. Thus, we conclude that the  $2.683 \pm 0.008$ -eV value measured in the current experiment should be considered to be the most accurate electron affinity for  $C_{60}$  to date.

The neutral  $C_{60}$  has the highest point-group symmetry ( $I_h$ ). Among its 174 vibrational degrees of freedom there are only two totally symmetric modes ( $A_g$ ).<sup>34,35</sup> If the  $C_{60}$  anion and neutral ground states were to have the same symmetry, only these two  $A_g$  modes would be active, which would give rise to a simple vibrational progression in the photoelectron spectra for the ground-state transition. However, as mentioned above, the ground state of  $C_{60}^-$  has a  ${}^2T_{1u}$  state under the  $I_h$  symmetry, which is subject to the Jahn-Teller effect. The  ${}^2T_{1u}$  electronic state could couple with any vibrations of  $H_g$  symmetry.<sup>23</sup> Thus, in addition to the two  $A_g$  modes, the eight  $H_g$  modes of  $C_{60}$  are also active through vibronic coupling in the  $C_{60}^-$  ground state, giving rise to the complicated vibrational structure in the photoelectron spectra. An expanded portion of the 355-nm spectrum is shown in Fig. 3, which is plotted in wave numbers with the 0-0 transition at

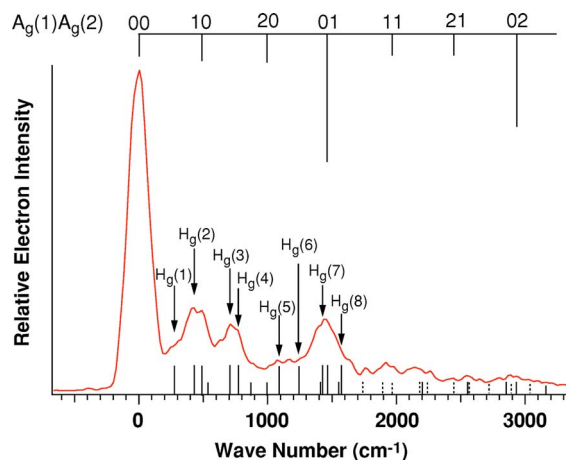


FIG. 3. Expanded portion of the 355-nm spectrum of cold  $C_{60}^-$ , showing details of the resolved vibrational structures. The spectrum is plotted in wave numbers with the 0-0 transition at 2.683 eV as the origin. The positions for the excitation of the two  $A_g$  modes are indicated at the top of the figure. The vertical lines in the figure depict the positions for the excitation of the two  $A_g$  and eight  $H_g$  modes. The short lines represent the overtone of each mode. The dashed lines show the combination bands of the  $H_g$  modes and one quantum of the  $A_g(2)$  mode.

2.683 eV as the origin. The peaks at 484 and 1452  $cm^{-1}$  correspond to the vibrational frequencies of the  $A_g(1)$  and  $A_g(2)$  modes of  $C_{60}$ .<sup>23,35</sup> In Fig. 3, the expected vibrational transitions for the two  $A_g$  modes and the eight  $H_g$  modes, as well as their overtones, are indicated with vertical lines, according to the calculated frequencies from Ref. 23. The current data provide clear evidence that all ten modes are active in the photodetachment transition.

In conclusion, we demonstrated that vibrationally cold anions can be produced using a cryogenic ion trap. The temperatures of trapped ions are controlled via collisions with a background gas in the ion trap, which is connected to a closed-cycle helium refrigerator (10–400 K). A relatively large anion  $C_{60}^-$  is used to test the cooling effect of the apparatus. We observed that vibrational hot bands in photoelectron spectra of  $C_{60}^-$  taken at a 70-K trapping temperature were completely eliminated with an estimated vibrational temperature of  $C_{60}^-$  to be  $<90$  K. The cold  $C_{60}^-$  photoelectron spectra yielded the well-resolved vibrational structures in photodetachment transitions to both the ground and the first excited state of  $C_{60}$ . A more accurate electron affinity of  $2.683 \pm 0.008$  eV was measured for  $C_{60}$ , as well as a more accurate excitation energy for the lowest triplet excited state of  $C_{60}$  ( $1.62 \pm 0.1$  eV), which can also be viewed as the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of  $C_{60}$ . Two totally symmetric modes ( $A_g$ ) and eight  $H_g$  modes were observed in the ground-state detachment transition, providing ideal data to evaluate the vibronic coupling in  $C_{60}^-$ .

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