ELSEVIER

International Journal of Mass Spectrometry 223–224 (2003) 695–701

International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Mass spectrometric study of $K^+ + C_{60}$ collisions

R. Deng, A. Clegg[1], O. Echt*

Department of Physics, University of New Hampshire, Durham, NH 03824, USA

Received 28 April 2002; accepted 21 June 2002

Abstract

We report on formation of endohedral metallofullerenes by collision of K^+ with C_{60} in the gas phase. Preparation of potassium ion emitters in a home-built furnace that reaches temperatures in excess of 1800 °C, and their performance, are discussed in detail. From the absence of $K@C_{60}{}^+$ in the mass spectra we estimate that the threshold energy for insertion of K^+ into C_{60} amounts to about 48 eV (lab energy). (Int J Mass Spectrom 223–224 (2003) 695–701)

Keywords: Metallofullerene; Endohedral; Insertion threshold; Alkali ion emitter

1. Introduction

A variety of applications are envisioned for endohedral metallofullerenes, in electronics, optics, and medicine [1–4]. For example, it has been suggested that $K@C_{60}$ enclosed in a C_{480} nanocapsule could be used as a non-volatile memory element [5]. However, production of endohedral metallofullerenes is generally inefficient, and the standard method of arc-evaporation followed by solvent-extraction has, with few exceptions [6,7], not led to C_{60}-based metallofullerenes.

Another avenue for production of $M@C_{60}$ is via gas-phase collisions at hyperthermal energies. This approach had originally been explored for formation of $He@C_{60}$ and $Ne@C_{60}$ (see [8] and references therein). While the yield will be miniscule, this method offers a chance to determine the energetics and dynamics of endohedral fullerenes. In this contribution we present a mass spectrometric study of collisions between a beam of potassium ions and a molecular beam of C_{60}. We also describe in detail the preparation of potassium ion emitters in a home-built furnace that safely achieves temperatures of 1800 °C in an inert gas atmosphere, and we characterize the performance of these emitters.

A number of previous studies of potassium-C_{60} at low collision energies have been reported; they resulted in formation of exohedral $KC_{60}{}^+$ [9–13]. Anderson and co-workers [14] were the first to investigate potassium-C_{60} collisions at higher energies in the gas phase. For energies exceeding 40 eV, they observed $K@C_n{}^+$ in which the K ion appears to be endohedral, with $n \leq 58$. $C_n{}^+$ with $n \leq 60$ appeared at somewhat lower energies. Campbell et al. [15] bombarded C_{60} films with K^+ and identified, for implantation energies exceeding roughly 40 eV, the formation of $K@C_{60}$ by thermal desorption and laser-desorption mass spectrometry.

Furthermore, the structure and energetics of $K@C_{60}$ have been the topic of several theoretical studies.

---

* Corresponding author. E-mail: olof.echt@unh.edu

[1] Present address: 328 Concord Stage Rd., Weare, NH 03821, USA.

PII S1387-3806(02)00941-7

There is qualitative agreement that the minimum energy position of K^+ is close to the center, much closer than for Li^+ and Na^+; the computed complexation energies range from 0.5 to 2.3 eV [16–20]. Some of these studies pertain to $K@C_{60}$ while others pertain to $(K@C_{60})^+$, but in both cases the charge of the caged atom would be very close to 1+, and little if any effect on the displacement and the complexation energy would be expected [17].

2. Experiment

A commercial ion emitter cartridge [21] was used. It consists of an indirectly heated, highly porous tungsten plug (6.3 mm diameter) into which aluminasilicate containing alkalis, or other metallic elements, are fused. Visual inspection of new, unused emitters reveals that a glassy, occasionally very rough, uneven layer of 1–2 mm thickness covers the tungsten plug. At temperatures around 1000 °C, a large fraction of the alkalis that are vaporized from these surfaces are positively charged due to surface ionization [22,23].

The ion emitters are exhausted after roughly 100 h of operation; we replenished potassium doped sources as follows: The emitter surface was coated with a paste that was made of de-ionized water into which powders of K_2CO_3, Al_2O_3, SiO_2 (STREM, purities 99+, 99+ and 99.8%, respectively) in the stoichiometric ratio 1:1:2 were mixed. The paste was allowed to dry on the emitter surface for at least 1 day in air under a dust-cover. Another two coatings were usually added to build thicker layers on the emitter surface.

The ion emitter cartridge is designed to achieve temperatures of 900–1200 °C; this does not suffice to fuse the powder [24]. Therefore, we built a furnace that safely reaches temperatures of 1800 °C in an argon atmosphere. In one run, the furnace was heated to a temperature exceeding 2200 °C, at which point it failed. The design was inspired by a furnace described by Webb and Miller [25]. Molybdenum sheet metal of 0.1 mm thickness is shaped into a cylinder of 12.7 mm diameter and 130 mm length. A few turns of Mo wire are wrapped around the cylinder to prevent it from unfolding. The edge of the Mo sheet metal on the inside of the cylinder is cut and bent so as to provide a platform in the center of the furnace that will support the ion emitter cartridge. Several layers of yttria textile [26], which has a melting temperature of 2410 °C, are wrapped around the molybdenum cylinder for thermal insulation.

This assembly, shown in Fig. 1, is then mounted vertically by inserting it into bores in two copper electrodes separated by about 120 mm. The electrodes are attached to copper rods of 6.3 mm diameter. Several Mo heat shields are mounted above (not shown in Fig. 1) and below the furnace. A gap of several millimeter between the yttria insulation and the copper

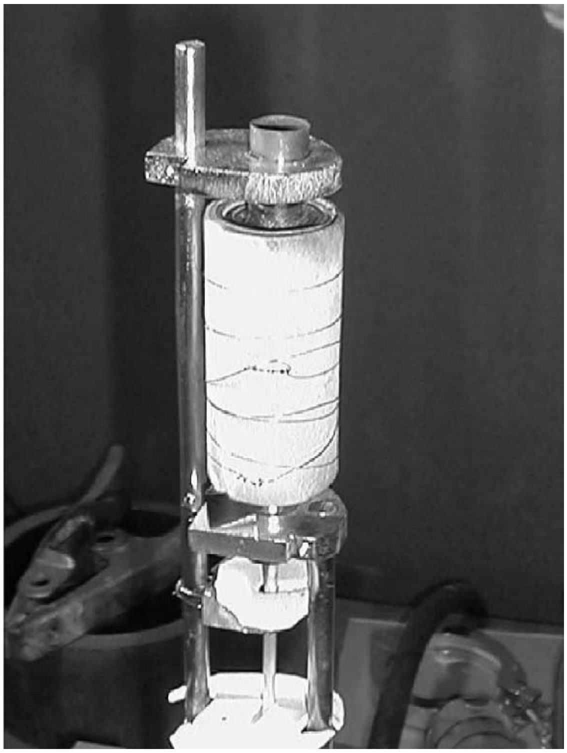

Fig. 1. Photograph of furnace that is used to replenish exhausted ion emitters. Shown are the molybdenum tube with yttria insulation wrapped around, the W–Re thermocouple inserted from below, and the copper electrodes used for support. Temperatures of 1800 °C in an atmosphere of argon are safely obtained near the center of the furnace.

electrodes is essential to provide a temperature gradient; else the copper electrodes get too hot and melt.

The Cu rods are epoxied into a flange made from ULTEM, a thermoplastic polyetherimide polymer. Also epoxied into this flange is a gas inlet, and a W5%Re–W26%Re thermocouple that extends into the furnace just below the platform. To operate the furnace in an inert gas atmosphere, the ULTEM flange is attached to the bottom of a 400 mm long, 50 mm diameter stainless steel tube supplied with KF flanges at both its ends. The tube and the KF flanges are water cooled from the outside.

The WRe thermocouple is calibrated by suspending a Pt wire in the center of the furnace and heating the assembly to successively higher temperatures until the Pt wire is, upon re-opening of the top flange, found to be molten. A current of 100–150 A from an ac supply is sufficient to reach the melting temperature of Pt at 1769 °C.

In the next step, the cartridge coated with the powder mix is lowered from the top into the center of the Mo furnace with help of thin Mo wires. The stainless steel tube is then added, flanged off and continuously purged with Ar (purity 99.999%). The temperature is increased gradually, over the course of 30 min, and then kept at 1650 °C for about 10 min. It is important to keep the molten material above its melting temperature long enough to eliminate CO_2 completely, else the material may flake off when re-heated [27]. After baking, the powder on the emitter surface had fused into a smooth, glass-like, slightly transparent matrix.

The emitter is then mounted in a home-built ion gun that accelerates, decelerates and focuses the ions into the center of the extraction region of a Wiley-McLaren time-of-flight mass spectrometer. Pulsed voltages are used to chop the metal ion beam. In the Wiley-McLaren lens the metal ion beam intersects a beam of C_{60} that emerges from a stainless steel Knudsen cell kept at 570 °C. Product ions from collisions or charge exchange reactions are accelerated by pulsed extraction potentials at a repetition rate of 6 kHz towards a microchannel plate detector at the end of a drift tube. The metal ion current and the C_{60} flux are monitored whenever the collision energy is varied; data presented here are corrected for any changes. These and many other details have been provided elsewhere [28]. Some preliminary data on the $K^+ + C_{60}$ system had been presented in an earlier report [29].

3. Results and discussion

We have tested the performance of the replenished ion emitters and compared them with that of new, commercial emitters. The maximum achievable ion current was determined by using a commercial ion gun [30]. The beam current was measured at a distance of about 5 cm on a circular target of about 2 cm diameter. The result for one source is shown in Fig. 2. A current of 400 nA at 20 eV, and 2.2 μA at 100 eV, is obtained. These values are at least as high as those obtained with commercial potassium sources. An accurate comparison, however, is made difficult by our lack of precise control over the temperature of the emitter surface.

Another important performance criterion is the purity of the ion beam. Fig. 3 displays time-of-flight mass spectra of three commercial sources, and of one potassium source replenished by us (labeled “UNH” in Fig. 3). Although the pulsed extraction fields of the TOF-MS may give rise to slight discrimination against light ions like Li^+, the spectra appear to

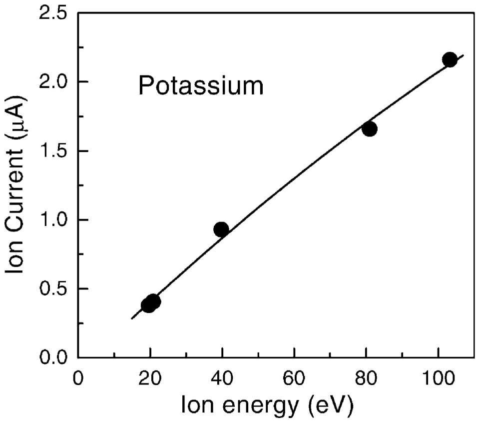

Fig. 2. Ion current of a replenished potassium ion emitter. The line is drawn to guide the eye.

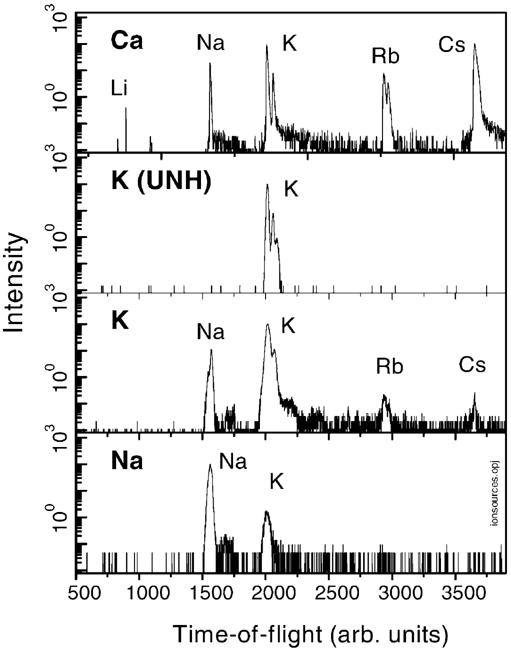

Fig. 3. Time-of-flight mass spectra of commercial sodium, potassium and calcium ion emitters, and a K source replenished by us (labeled K UNH). Note the difference in the impurity content (the ordinate is logarithmic, all spectra cover 5 orders of magnitude), and the absence of any Ca^+ (mass 40 u) in the "calcium" spectrum. Spectra were recorded at different times and with different settings; differences in resolution and background level are not considered significant.

correctly and reproducibly reflect the intensities of heavier alkalis within a factor of two. The results are as follows:

1. The commercial Na source carries 1% of K^+ impurities; other elements occur at levels $\leq$0.01%.
2. The commercial K source carries 10% of Na^+ impurities, plus Rb^+ and Cs^+ at levels of 0.1%.
3. The K source replenished by us carries no more than 0.01% of impurities.
4. The commercial Ca source does not deliver any significant amounts of Ca^+ (mass 40 u) under our conditions; instead it delivers intense beams of Na^+, K^+ (the isotopes K-39 (93% natural abundance) and K-41 (7%) are well resolved in the spectrum), Cs^+, plus smaller amounts of Li^+ (isotopes Li-6 and Li-7) and Rb^+ (isotopes Rb-85 and Rb-87).

The results may, to some extent, depend on the temperature at which the sources are operated, and the amount of time they have been in operation. For example, the manufacturer specifies impurities on the order of 1% for its Li sources that are said to decline to the 0.01% level after a few hours of operation. Our experience with Na and K sources indicates that this underestimates the impurity level. Furthermore, the spectrum of the K source replenished by us was recorded after less than 1 h of operation.

The manufacturer of the Ca source has not been able to provide an explanation for the large amount of alkali ions and complete absence of Ca^+. We have also tested a Sr source from the same manufacturer and found copious amounts of Li^+ plus other alkalis but no, or very little, Sr^+.

In Fig. 4 we present the yield of selected ions produced by $K^+ + C_{60}$ collisions, namely $K@C_{56}{}^+$, $K@C_{54}{}^+$, $C_{60}{}^+$, and $C_{58}{}^+$. Of these, $C_{60}{}^+$ is the most

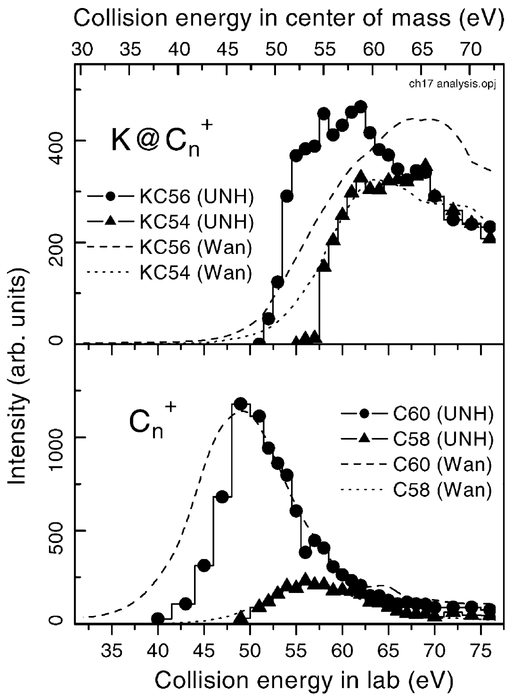

Fig. 4. Solid dots: yield of selected ions produced in collisions $K^+ + C_{60}$. Dashed lines represent results reported by Wan et al. [14], normalized to the same peak intensities as our data.

intense ion, followed by $K@C_{56}{}^{+}$ and $K@C_{54}{}^{+}$. $K@C_{58}{}^{+}$ is observed as well, but its yield reaches no more than 20% of the yield of $K@C_{56}{}^{+}$ at its respective maximum. $K@C_{60}{}^{+}$ is not observed at all, in agreement with results reported by Anderson and co-workers (a small signal of $K@C_{60}{}^{+}$ that they observed at higher collision energies appeared to arise from $K^{+} + C_{70}$ collisions).

In Fig. 4 we contrast our data with those reported by Wan et al. [14]. Their ion yields are normalized, for each ion species, to match the peak intensities observed in our work. The ratio of peak intensities that we obtain for the four different species deviates significantly from those reported by Wan et al. For example, we find $K@C_{56}{}^{+}$ and $K@C_{54}{}^{+}$ in a ratio of about 1.4, while their value is 0.6.

One major difference between our experimental setup, and the setup used by Wan et al. [14], is the time scale over which an ion has to survive after its collisional formation, in order to become observable in the mass spectra. In our experiment this time is about 10 μs [28], while it is 0.5–5 ms in their study. For statistical decay reactions, an increase in time will result in a "kinetic shift" of breakdown energies to lower values. Such a shift is not observed in the comparison of data recorded on these two widely different time scales (Fig. 4). It appears that, in agreement with an earlier comparison of data for $Na@C_{60}{}^{+}$, the absence of such a shift arises from a combination of two factors: (i) a broader distribution of collision energies in the study by Wan et al., and (ii) a suppression of the kinetic shift by radiative cooling. Radiative cooling is known to compete with dissociation for neutral and positively charged fullerenes; it will quench dissociation on time scales of about 10^{-5} s and larger [28,31,32].

Another difference appears in the ion yield at low energies. In our data, the yield rises much more steeply beyond an energy threshold that is, generally, higher than reported by Wan et al. Those authors reported a common threshold of about 40 eV for $K@C_{n}{}^{+}$ ions ($n = 58, 56, 54$) while we find, approximately, 51 eV (lab energy) for the appearance of $K@C_{56}{}^{+}$; the appearance of $K@C_{54}{}^{+}$ is shifted upwards by about 6 eV. One possible cause for these differences would be, again, a broader distribution of collision energies in the study by Wan et al.

It should be noted, though, that the appearance energies of the ions discussed here reflect a variety of processes, not necessarily the energy threshold for insertion of K^{+} into C_{60}. For example, the $C_{60}{}^{+}$ ion has been postulated to originate from thermionic emission of collisionally excited C_{60} [14]. Thermionic emission is a statistical process, hence the appearance energy of $C_{60}{}^{+}$ will exhibit kinetic shifts (limited by radiative cooling); its value will decrease when the time scale of the experiment is increased [33], in agreement with the trend observed in Fig. 4.

We now attempt to estimate the threshold energy for insertion of K^{+} into C_{60}, based on our present data and on a numerical model that provided an excellent fit to the energy dependence of the ion yield of $Na@C_{60}{}^{+}$ [28] over a wide range of collision energies. In that model we assumed an Arrhenius pre-exponential of $\nu_0 = 5 \times 10^{19}\,\mathrm{s}^{-1}$. An activation energy of 10.17 eV was derived for loss of C_2, in excellent agreement with several recent values for $C_{60}{}^{+}$ [34].

The absence of any trace of $K@C_{60}{}^{+}$ in our spectra does not mean that such a species does not form, but that the insertion threshold is too high, and the ion lifetime too short, for the ion to be observed on the time scale of the experiment (unless the species is formed in a matrix where it may quickly de-excite [15]). We estimate that a survival probability of 10% or less at its formation threshold energy E_{th} will prevent the successful detection of $K@C_{60}{}^{+}$. Ten percent may seem high, but the survival probability will quickly decline with increasing collision energy to, for example, 1% when the collision energy exceeds the threshold by 3 eV. Our model predicts a 10% survival probability with respect to C_2 loss when the vibrational excitation energy in $K@C_{60}{}^{+}$ reaches 52.9 eV. The adduct ion will carry this excess energy if produced in collisions at 48.1 eV (lab energy), or 45.7 eV in the center-of-mass. Here we assume that the complexation energy of $K@C_{60}{}^{+}$ is 2 eV [16–20], and we take into account the internal (vibrational) energy of C_{60} effusing from a source at 570 °C.

Given the small survival probability of $K@C_{60}{}^{+}$, the insertion threshold will become the appearance energy of its daughter ion, $K@C_{58}{}^{+}$. This ion has a very low yield, indicating that it decays rapidly into $K@C_{56}{}^{+}$ which is observed with an appearance energy of 51 eV (lab energy), i.e., 3 eV above the appearance energy of its postulated parent ion, $K@C_{58}{}^{+}$. This difference of 3 eV is somewhat less than the difference of about 6 eV that we observe between the appearance of $K@C_{56}{}^{+}$ and its daughter, $K@C_{54}{}^{+}$. The same difference of 6 eV is also observed in the appearance energies of fullerene ions in electron impact ionization studies [35]. However, given that the insertion threshold of 48.1 eV estimated above did not invoke any experimental data other than the fact that $K@C_{60}{}^{+}$ is not observed, we consider the agreement satisfactory. On the other hand, the model could not possibly explain the formation of $K@C_n{}^{+}$ ($n \leq 58$) at lab energies as low as 40 eV [14], because the adduct ion would be long-lived at this energy and hence be observable.

How does our estimate for the insertion threshold compare with other experimental and theoretical work? As mentioned before, Wan et al. place the appearance energy for $K@C_{58}{}^{+}$, $K@C_{56}{}^{+}$, and $K@C_{54}{}^{+}$ at 40 eV [14], but it seems that the broader energy distribution of their metal ion beam may have caused them to underestimate the insertion threshold [28]. Caldwell et al. [36] studied the formation of complexes in collisions of $C_{60}{}^{+}$ with Ar, which is isoelectronic with K^{+}. They observed only odd-carbon species, $ArC_x{}^{+}$ with $x \leq 55$. However, the center-of-mass collision energy in these experiments was 421 eV, an order of magnitude higher than in our present work. Collisional fragmentation of $Ar@C_{60}{}^{+}$ has been reported by two groups [37,38], but these experiments provide no information on the insertion threshold.

Cui et al. [39] have performed a molecular dynamics study of inert gases colliding with C_{60}. They report a threshold of 48 eV for insertion of Ar through the center of a six-membered ring, in good agreement with our estimate of 45.7 eV (center-of-mass energy). C–C bonds are broken in this process and the structure does not fully relax within the time scale of the simulation, 328 fs. On the other hand, Shiga et al. [40] find, in an ab initio study of C_{60} collisions with Kr, K, and other atoms, that the fullerene network relaxes within 30 fs after insertion of krypton at 140 eV, whereas insertion of potassium at 100 eV leads to a long-lived defect. These and other studies frequently refer to a multistep "window" mechanism that would make insertion possible at lower energies through a defective site that is supposed to be created by the previous impact of another atom [41–43]. However, this multi-step mechanism is not a viable option under our experimental conditions, because C_{60} emerging from a thermal source is unlikely to have any structural defects before collisions, and multiple collisions of metal ions with one and the same target molecule are exceedingly unlikely.

In conclusion, we have presented the yield of fullerene and potassium-fullerene ions that are formed in collisions of K^{+} with C_{60} in the gas phase. We estimate the threshold energy for insertion of K^{+} to be 48.1 eV (45.7 eV in the center-of-mass system), based on the fact that no ion signal at the mass of $K@C_{60}{}^{+}$ is observed over the whole range of collision energies, whereas long-lived $K@C_n$ $n \leq 58$, is formed.

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. 9507959. We thank P.J. Beckman for help during the early stages of the project.

References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.
[2] H. Shinohara, Rep. Prog. Phys. 63 (2000) 843.
[3] S.Y. Liu, S.Q. Sun, J. Organomet. Chem. 599 (2000) 74.
[4] L.J. Wilson, D.W. Cagle, T.P. Thrash, S.J. Kennel, S. Mirzadeh, J.M. Alford, G.J. Ehrhardt, Coordination Chem. Rev. 192 (1999) 199.
[5] Y.K. Kwon, D. Tomanek, S. Iijima, Phys. Rev. Lett. 82 (1999) 1470.
[6] T. Ogawa, T. Sugai, H. Shinohara, J. Am. Chem. Soc. 122 (2000) 3538.

[7] T. Kanbara, Y. Kubozono, Y. Takabayashi, S. Fujiki, S. Iida, Y. Haruyama, S. Kashino, S. Emura, T. Akasaka, Phys. Rev. B 6411 (2001) 3403.
[8] H. Schwarz, T. Weiske, D.K. Böhme, J. Hrusak, in: W.E. Billups, M.A. Ciufolini (Eds.), Buckminsterfullerenes, VCH Publishers, New York, 1993, p. 257.
[9] L.S. Wang, O. Chesnovsky, R.E. Smalley, J.P. Carpenter, S.J. Hwu, J. Chem. Phys. 96 (1992) 4028.
[10] P. Weis, R.D. Beck, G. Bräuchle, M.M. Kappes, J. Chem. Phys. 100 (1994) 5684.
[11] U. Zimmermann, N. Malinowski, A. Burkhardt, T.P. Martin, Carbon 33 (1995) 995.
[12] S. Pollack, D. Cameron, M. Rokni, W. Hill, J.H. Parks, Chem. Phys. Lett. 256 (1996) 101.
[13] D. Rayane, R. Antoine, P. Dugourd, E. Benichou, A.R. Allouche, M. Aubert-Frecon, M. Broyer, Phys. Rev. Lett. 84 (2000) 1962.
[14] Z. Wan, J.F. Christian, Y. Basir, S.L. Anderson, J. Chem. Phys. 99 (1993) 5858.
[15] E.E.B. Campbell, R. Tellgmann, N. Krawez, I.V. Hertel, J. Phys. Chem. Solids 58 (1997) 1763.
[16] Y.S. Li, D. Tomanek, Chem. Phys. Lett. 221 (1994) 453.
[17] J. Cioslowski, Electronic Structure Calculations on Fullerenes and Their Derivations, Oxford University Press, Oxford, 1995.
[18] F.D. Proft, C.V. Alsenov, P. Geerlings, J. Phys. Chem. 100 (1996) 7440.
[19] E. Broclawik, A. Eilmes, J. Chem. Phys. 108 (1998) 3498.
[20] A. Ruiz, J. Hernandezrojas, J. Breton, J.M.G. Llorente, J. Chem. Phys. 109 (1998) 3573.
[21] Model STD-250 from Spectra-Mat, Watsonville, CA.
[22] G.D. Alton, in: F.B. Dunning, R.G. Hulet (Eds.), Experimental Methods in the Physical Sciences, vol. 29A, Academic Press, San Diego, 1995, p. 69.
[23] B.H. Wolf, in: B.H. Wolf (Ed.), Handbook of Ion Sources, CRC Press, Boca Raton, 1995.
[24] J.P. Blewett, E.J. Jones, Phys. Rev. B 50 (1936) 464.
[25] G.W. Webb, R.E. Miller, Rev. Sci. Instr. 44 (1973) 1542.
[26] Model ZYF-50, Zircar Products, Florida, NY.
[27] S.K. Allison, M. Kamegai, Rev. Sci. Instr. 32 (1961) 1090.
[28] R. Deng, O. Echt, Chem. Phys. Lett. 353 (2002) 11.
[29] R. Deng, R. MacCrimmon, O. Echt, in: P. Jena, S.N. Khanna, B.K. Rao (Eds.), Cluster and Nanostructure Interfaces, World Scientific, Singapore, 2000, p. 437.
[30] Model HWIG-250, Heatwave, California.
[31] J. Laskin, C. Lifshitz, Chem. Phys. Lett. 277 (1997) 564.
[32] S. Tomita, J.U. Andersen, C. Gottrup, P. Hvelplund, U.V. Pedersen, Phys. Rev. Lett. 87 (2001) 073401.
[33] J. Laskin, J.M. Behm, K.R. Lykke, C. Lifshitz, Chem. Phys. Lett. 252 (1996) 277.
[34] S. Matt, O. Echt, P. Scheier, T.D. Märk, Chem. Phys. Lett. 348 (2001) 194.
[35] S. Matt, O. Echt, R. Wörgötter, P. Scheier, C.E. Klots, T.D. Märk, Int. J. Mass Spectrom. Ion Process. 167/168 (1997) 753.
[36] K.A. Caldwell, D.E. Giblin, M.L. Gross, J. Am. Chem. Soc. 114 (1992) 3743.
[37] C. Brink, P. Hvelplund, H. Shen, H.A. Jimenez-Vazquez, R.J. Cross, M. Saunders, Chem. Phys. Lett. 286 (1998) 28.
[38] J. Laskin, T. Peres, A. Khong, H.A. Jimenez-Vazquez, R.J. Cross, M. Saunders, D.S. Bethune, M.S. DeVries, C. Lifshitz, Int. J. Mass Spectrom. Ion Process. 187 (1999) 61.
[39] F.Z. Cui, D.X. Liao, H.D. Li, Phys. Lett. A 195 (1994) 156.
[40] K. Shiga, K. Ohno, Y. Maruyama, Y. Kawazoe, T. Ohtsuki, Model. Simul. Mater. Sci. Eng. 7 (1999) 621.
[41] R.L. Murry, G.E. Scuseria, Science 263 (1994) 791.
[42] H. Sprang, A. Mahlkow, E.E.B. Campbell, Chem. Phys. Lett. 227 (1994) 91.
[43] M. Saunders, R.J. Cross, H.A. Jimenez-Vazquez, R. Shimshi, A. Khong, Science 271 (1996) 1693.