Eur. Phys. J. D **16**, 365–368 (2001)

THE EUROPEAN
PHYSICAL JOURNAL D
EDP Sciences

Molecular beam deflection experiments on mixed clusters

Permanent dipole of transition metal-C_{60} compounds

I. Compagnon, R. Antoine, D. Rayane, Ph. Dugourd[a], and M. Broyer

Laboratoire de Spectrométrie Ionique et Moléculaire[b], Université Lyon I et CNRS, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France

Received 22 November 2000

Abstract. Gas phase Ti-C_{60} clusters are studied by molecular beam electric deflection. The permanent dipole moment of the TiC_{60} molecule is determined. It is equal to 8.1 ± 1.5 D. This dipole is due to a transfer of electron from the transition metal atom to the C_{60} cage. No dipole is observed for $Ti(C_{60})_2$ molecules. This is in agreement with the symmetrical dumbbell-like structure that has been previously proposed.

PACS. 33.15.Kr Electric and magnetic moments (and derivatives), polarizability, and magnetic susceptibility – 36.40.Cg Electronic and magnetic properties of clusters – 61.48.+c Fullerenes and fullerene-related materials

1 Introduction

Since the discovery of C_{60}, a versatile derivatization chemistry of fullerenes has been developed [1]. Transition metal-fullerene complexes have attracted much fascination due to their potentiality for catalytic activity and the possibility of forming new supermolecular compounds. Mass spectrometry studies have shown that transition metal-C_{60} complexes can be produced in the gas phase [2–4]. Laser-induced transformations from transition metal fullerenes to metal-carbide and met-car compounds have been evidenced by Martin and coll. [5]. Kaya and coll. have used absorption reactivity in a conventional flow-tube reactor to obtain information on the structure of these clusters. The reactivity of $Ti_n(C_{60})_{n+1}$ clusters toward O_2 and CO is in favor of a multiple dumbbell structure, in which transition metal atoms and C_{60} are alternatively stacked [6,7]. In this article, we report the first measurement of the permanent dipole of transition metal-C_{60} compounds. The results obtained by the molecular beam deflection technique give new information on the electronic and geometric structures of small titanium fullerene clusters.

2 Experimental set up

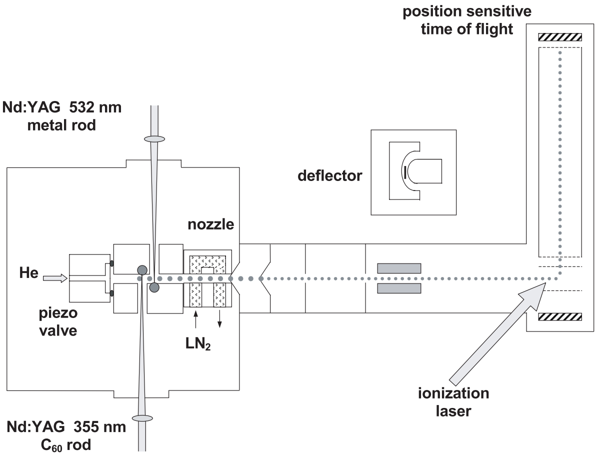

Fig. 1. Schematic of the experimental set up.

Figure 1 shows a schematic of our experimental set up. It consists of a laser vaporization source, an electric deflector, and a position sensitive time of flight mass spectrometer. Titanium-C_{60} clusters are generated in a laser vaporization source with two rods and two pulsed lasers. We use the third harmonic of a Nd:YAG to desorb a C_{60} rod (> 99.9% purchased from MER corp.). A low laser power is used in order to avoid any fragmentation of the fullerenes. The second harmonic of a Nd:YAG is focused on a titanium rod. This laser is fired with a time delay of a few microseconds after the first laser pulse. The time delays of both lasers are synchronized on a piezo-electric pulsed valve. Helium is used as carrier gas. The clusters leave the source through a 5 cm long nozzle which can be cooled down to 85 K. The molecular beam is skimmed and tightly collimated by two slits. It is deflected with a “two-wire” electric field configuration. The clusters are ionized 1 m after the deflector in the extraction region

---

[a] e-mail: `dugourd@lasim.univ-lyon1.fr`

[b] UMR 5579 du CNRS

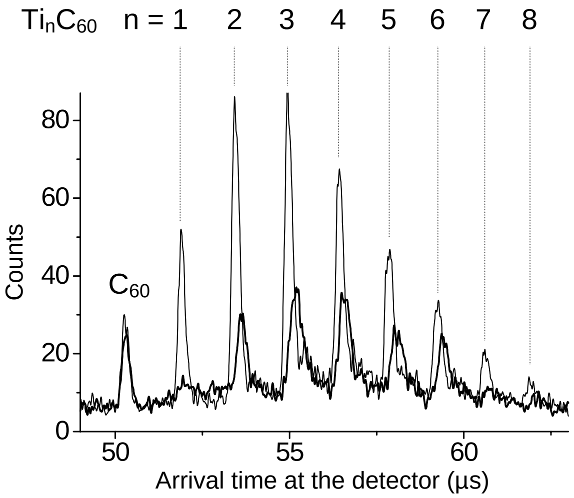

Fig. 2. Ti_nC_{60} mass spectra obtained at $T = 85$ K without (thin line) and with (thick line) an electric field in the deviator equal to 1.5×10^7 V/m.

of the position-sensitive time of flight mass spectrometer. The deviation d of a molecule, is determined by comparing the arrival time at the detector measured with the electric field in the deflector to the arrival time measured without electric field in the deflector. In first approximation, the difference in time Δt is proportional to d. The deviation d for a molecule of mass m with a velocity v is given by:

$$d = \frac{K\langle f\rangle}{2mv^2}$$

where K is a geometric factor and $\langle f\rangle$ is the average force in the deviator. The velocity is selected and measured with a mechanical chopper.

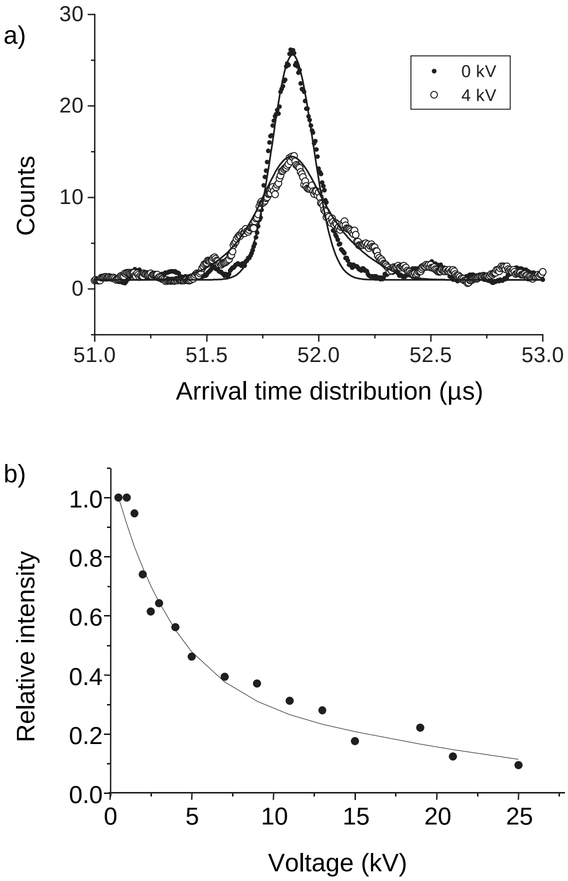

Fig. 3. a) Arrival time distribution profiles of TiC_{60}. (●) Experimental profile without deviation (0 kV). (○) Experimental profile with a voltage of 4 kV across the deviator; (—) results of simulations at 0 kV and 4 kV for a dipole moment of 8.1 D. b) Variation of the intensity at the maximum of the profile of the TiC_{60} molecule. (●) experimental results, (—) results of simulations for a dipole moment of 8.1 D.

3 Results and discussion

3.1 Ti_nC_{60} clusters

Figure 2 shows mass spectra of Ti_nC_{60} clusters, recorded with a nozzle temperature of 85 K. An ArF excimer laser (193 nm) is used for the ionization. C_{60} with zero to height titanium atoms are observed in this figure. The two spectra in Fig. 2 are recorded under the same source and time delay conditions, without and with an electric field ($F = 1.5 \times 10^7$ V/m) in the deflector. For C_{60}, there is almost no change. For fullerenes with titanium atoms, the shape of the arrival time distribution (ATD) profile is strongly modified. For the TiC_{60} molecule, a strong broadening of the signal is observed. For Ti_nC_{60} clusters with $n = 2$-7, large shifts toward longer arrival time and a slight broadening of the peaks are observed.

Fig. 3a shows the ATD profile obtained for the TiC_{60} molecule with 4 kV across the deviator ($F = 0.24 \times 10^7$ V/m). A symmetrical broadening of the profile and a decrease in the intensity on the beam axis are observed. In order to simulate the rotational motion of the molecule in the electric field, the rotational constants of the TiC_{60} molecule are needed. The TiC_{60} geometry was optimized at the ZINDO level. The geometric parameters of C_{60} were frozen and the titanium atom was put in front of an hexagon ring. The optimized geometry of TiC_{60} molecule is found with the Ti atom at the center of the hexagon (C_{3v} symmetry) and at a distance of 1.17 Å from the center of the ring. For the structure obtained from the ZINDO optimization, the rotational constants are $A = B = 0.0025$ cm^{-1} and $C = 0.0029$ cm^{-1}. The motion of the TiC_{60} molecule in a static electric field is similar to the mechanical motion of an heavy symmetric top pendulum [8]. Simulations of ATD profiles are obtained through an adiabatic classical approach [9]. The results of the simulation (for a dipole moment of 8.1 D) are plotted in Fig. 3a. There is a good agreement between the experimental profile and the calculated profile. To determine the value of the permanent dipole moment with a good precision, we have systematically measured the intensity at the maximum of the peak as a function of the electric field. Experimental values are reported in Fig. 3b.

A strong decrease is observed. The best fit is obtained for $\mu = 8.1 \pm 1.5$ D and is plotted in Fig. 3b. Note that the results of the fit are not very sensitive to the value of the equilibrium distance between Ti and the C_{60} cage.

Titanium is known to strongly bind to carbon. The formation of titanium carbide is thermodynamically favorable [10], and Ti_nC_{60} clusters form metal carbide under heating [5]. The transition metal atom and C_{60} may form a π complex compound involving a metal aromatic ring interaction. Indeed, theoretical and experimental works have shown that C_{60} may behave like a η^6-ligand (where the notation η^6 is conventionally used to signify that the 6 carbon atoms of the ring are bound to the metal atom) [11]. An almost full transfer of electron from the Ti atom to the C_{60} cage is predicted. This is in agreement with the large dipole value that we have measured.

We have calculated the value of the dipole moment at the HF level for the structure obtained from the ZINDO optimization. For C atom, we used the STO-3G basis and for the Ti atom, the Stuttgart effective core potential (EPC10MDF [12]). The calculated value is 7.0 D. This value is in good agreement with the experimental value.

We now discuss the case of several titanium atoms on the fullerene cage. In Fig. 2, strong deviations superimposed to a broadening of the ATD profiles are observed. Large deviations have already been observed for alkali-C_{60} clusters. There were related to the non-rigidity of the molecules [13]. The alkali atom and therefore the dipole moment can move freely on the surface of the cage. There is a statistical orientation of the dipole in the electric field, leading to a large polarizability given by the Langevin formula $\alpha = \frac{\mu^2}{3kT}$, where μ is the dipole of the molecule for an equilibrium structure. For a single titanium atom on the cage, there is no shift of the ATD profiles. The molecule is rigid. With several atoms, large shifts are observed. The cluster has a permanent dipole and is not rigid. This suggests that the titanium atoms are not regularly distributed on hexagons, but form a metal cluster. The bonding of the metal cluster to the cage seems to be less rigid than the bonding of a single atom. The particular rigidity of the TiC_{60} molecule may be related to the high stability of the η^6-bonding.

3.2 $Ti_n(C_{60})_2$ clusters

Fig. 4 shows mass spectra of $Ti_n(C_{60})_2$ recorded with the same conditions as in Fig. 2. $(C_{60})_2$ with one to about ten atoms of titanium are observed. ATD profiles without and with electric field in the deviator ($V = 25$ kV) are different from those obtained for $Ti_n(C_{60})$ clusters. The electric field has a weak effect on the ATD profiles. For $Ti(C_{60})_2$ molecule, we observe a shift without any broadening (Fig. 5). This has to be compared to Fig. 3a) where a significant broadening is observed even at $V = 4$ kV. $Ti(C_{60})_2$ has no or a very weak dipole moment. The absence of permanent dipole shows that $Ti(C_{60})_2$ has a symmetrical structure. This is in agreement with the structure proposed in the literature [7] which is a linear geometry where the Ti atom is located between the two C_{60}. In Fig. 5 the shift in arrival time for $Ti(C_{60})_2$ molecule is 90 ns. This corresponds to a polarizability of 360 ± 150 Å^3. These experiments were performed with helium as carrier gas. The velocity of the beam was high and the shift due to the polarizability small. This explains the large incertitude on this value. This polarizability is higher than the polarizability that one obtains from the sum of the electronic polarizability of each constituent (≈ 175 Å^3) [14, 15]. Calculations from Saito *et al.* predict that the band structure of η^6-$(C_{60})_n Ti_n$ is metallic and that there is a delocalization of the *d* electrons of titanium through the LUMO of C_{60} [16]. The relatively large polarizability of $Ti(C_{60})_2$ molecule may be due to the occurrence of this delocalization along the molecular axis.

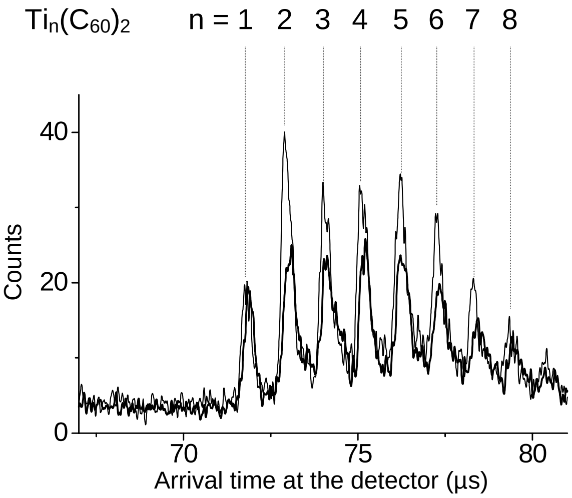

Fig. 4. $Ti_n(C_{60})_2$ mass spectra obtained without (thin line) and with (thick line) an electric field in the deviator equal to 1.5×10^7 V/m.

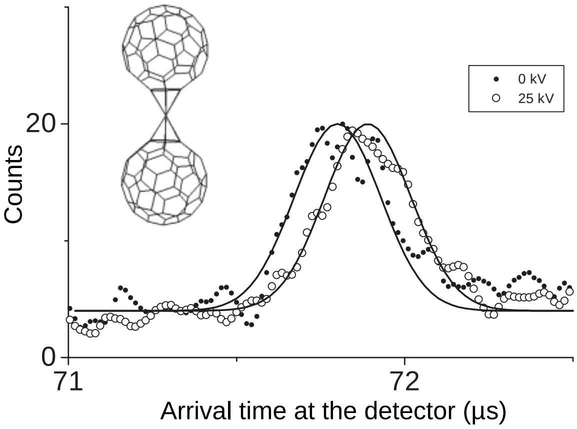

Fig. 5. Arrival time distribution profiles of $Ti(C_{60})_2$. (•) Experimental profile without deviation (0 kV). (◦) Experimental profile with a voltage of 25 kV (1.5×10^7) across the deviator. (—) fit of the experimental data with a Gaussian function. The insert shows the proposed dumbell-like structure for the $Ti(C_{60})_2$ molecule.

For molecules with more titanium atoms, we observe a small shift of the peaks and a slight broadening. The shifts are in the range of the one measured for $Ti(C_{60})_2$. The molecules have a polarizability close to the polarizability of $Ti(C_{60})_2$ and a small dipole (smaller than Ti_nC_{60} clusters). This is in qualitative agreement with a titanium cluster with two fullerenes bound on opposite sides.

4 conclusion

We have studied Ti_nC_{60} and $Ti(C_{60})_2$ clusters by molecular beam deflection (MBD) experiments. The permanent dipole moment of the TiC_{60} molecule has been determined. A value of 8.1 ± 1.5 D is obtained. For clusters with several titanium atoms, MBD experiments are in favor of a Ti cluster bound to the C_{60} cage. We have observed no permanent dipole for $Ti(C_{60})_2$. The absence of permanent dipole moment is in agreement with a linear structure with a titanium atom at the center of the two C_{60} fullerenes, *i.e.* dumbbell structures.

We gratefully acknowledge A.R. Allouche's help with *ab initio* calculations.

References

1. R. Taylor, *The Chemistry of Fullerenes* (World Sientific Publishing Co, Singapore, 1995).
2. Y. Huang, B.S. Freiser, J. Am. Chem. Soc. **113**, 8166 (1991).
3. L.M. Roth, Y. Huang, J.T. Schwedler, C.J. Cassady, D. Ben-Amotz, B. Kahr, B.S. Freiser, J. Am. Chem. Soc. **113**, 6298 (1991).
4. A. Nakajima, K. Kaya, J. Phys. Chem. A **104**, 176 (2000).
5. F. Tast, N. Malinowski, S. Franck, M. Heinebrodt, I.M.L. Billas, T.P. Martin, Phys. Rev. Lett **77**, 3529 (1996).
6. A. Nakajima, S. Nagao, H. Takeda, T. Kurikawa, K. Kaya, J. Chem. Phys. **107**, 6491 (1997).
7. S. Nagao, T. Kurikawa, K. Miyajima, A. Nakajima, K. Kaya, J. Phys. Chem. A **102**, 4495 (1998).
8. H. Goldstein, *Classical Mechanics* (Addison-Wessley Publishing Company, MA, 1980).
9. P. Dugourd, I. Compagnon, F. Lepine, R. Antoine, D. Rayane, M. Broyer, Chem. Phys. Lett. **336**, 511 (2001).
10. T. Tachibana, B.E. Williams, J.T. Glass, Phys. Rev. B **45**, 11975 (1992).
11. J.R. Rogers, D.S. Marynick, Chem. Phys. Lett. **205**, 197 (1993).
12. M. Dolg, U. Wedig, H. Stoll, H. Preuss, J. Chem. Phys. **86**, 866 (1987).
13. D. Rayane, R. Antoine, P. Dugourd, E. Benichou, A.R. Allouche, M. Aubert-Frecon, M. Broyer, Phys. Rev. Lett. **84**, 1962 (2000).
14. E.J. Reader, C.H. Corliss, *CRC Handbook of chemistry* (CRC Press, Boca Raton, FL, 1998).
15. R. Antoine, P. Dugourd, D. Rayane, E. Benichou, M. Broyer, F. Chandezon, C. Guet, J. Chem. Phys. **110**, 9771 (1999).
16. T. Saito, Y. Akita, H. Kobayashi, K. Tanaka, Synthetic Metals **108**, 67 (2000).