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Charge transfer in collisions involving multiply charged C_{60} molecules

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Abstract. Electron capture in collisions of C_{60}^{2+} and C_{60}^{3+} molecular ions with atomic and molecular gases has been studied at impact energies around 100 keV. The cross-section dependence on the target-ionization potentials is discussed, and a simple over-barrier model is evoked to explain the energy dependences. The cross sections for endothermic processes are discussed in the light of a simple two-state model, and a general understanding of their behaviour is obtained.

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1. Introduction

Charge transfer or electron capture in collisions between energetic ions and static atoms is a classical discipline in atomic physics. In low-velocity collisions, the charge state of the projectile ion and the ionization energy of the target atom are decisive parameters. Several studies of charge transfer in collisions between multiply charged fullerene ions and molecular and atomic targets have been reported recently [1–4], but little is known about absolute values of the cross sections for charge transfer. At thermal energies, the selected-ion flow tube technique [2] and the Fourier-transform ion cyclotron resonance method [3] have been used for 'bracketing' experiments. The purpose of these experiments [2, 3] was to determine the ionization potentials of C_{60} ions of various charge states. There is good agreement about the first ionization potential of C_{60}, but the second and higher potentials have caused problems. Bracketing experiments for multiply charged C_{60} ions gave values which are lower than values obtained by translational-energy loss in charge-stripping reactions [5] or by photon-ionization experiments [6, 7]. This controversy seems to have been solved by Petrie et al. [8]. They took into account the effect of Coulomb repulsion in the final state and suggested that the ionization potentials of C_{60} have the values $I_I = 7.60\ \text{eV} \pm 0.2\ \text{eV}$, $I_{II} = 11.80 \pm 0.5\ \text{eV}$, $I_{III} = 15.6 \pm 0.5\ \text{eV}$, and $I_{IV} = 19.5 \pm 0.5\ \text{eV}$.

We have studied the reactions

$$C_{60}^{2+} + X \rightarrow C_{60}^{+} + X^{+} \tag{1}$$

and

$$C_{60}^{3+} + X \rightarrow C_{60}^{2+} + X^{+} \tag{2}$$

at energies around 100 keV for the target gases NO ($I = 9.264$ eV), Xe ($I = 12.13$ eV), Kr ($I = 14.00$ eV), H_2 ($I = 15.43$ eV), Ar ($I = 15.76$ eV), and He ($I = 24.58$ eV). Some of the collisions are endothermic and some are exothermic. Which is which is most easily observed experimentally from the energy dependence of the cross section. For an endothermic process, the charge-transfer cross section increases with energy at low energies, while it normally decreases for an exothermic collision process. As discussed by Petrie et al. [8], this simple picture does not apply for multiply charged ions since the Coulomb barrier in the final state has to be taken into account. In the present communication, we treat this problem in the over-barrier model originally due to Bohr and Lindhard [9] and introduced in the field of collisions with multiply charged ions by Ryufuku et al. [10]. In this model, the Coulomb interaction results in a linear Stark shift of the ionic energy levels under the influence of a nearby ion. This simple approach is found to give a satisfactory explanation of the observed energy dependences of the charge-transfer cross sections.

The dependence of the charge-transfer cross sections on the target-ionization potential for endothermic processes has been estimated by the model two-state picture due to Rapp and Francis [11], and reasonable agreement with experimental values is obtained.

2. Experimental

The experimental setup is shown in Fig. 1. C_{60}^{2+} or C_{60}^{3+} ions were generated in a plasma ion source [12] and

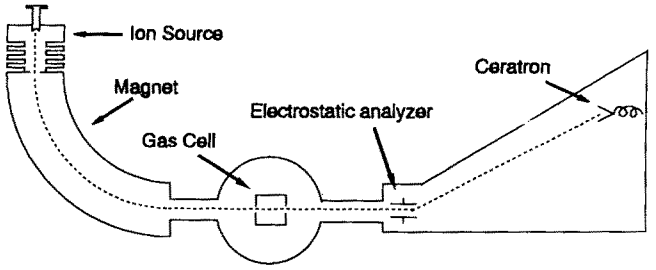

Fig. 1. Experimental setup

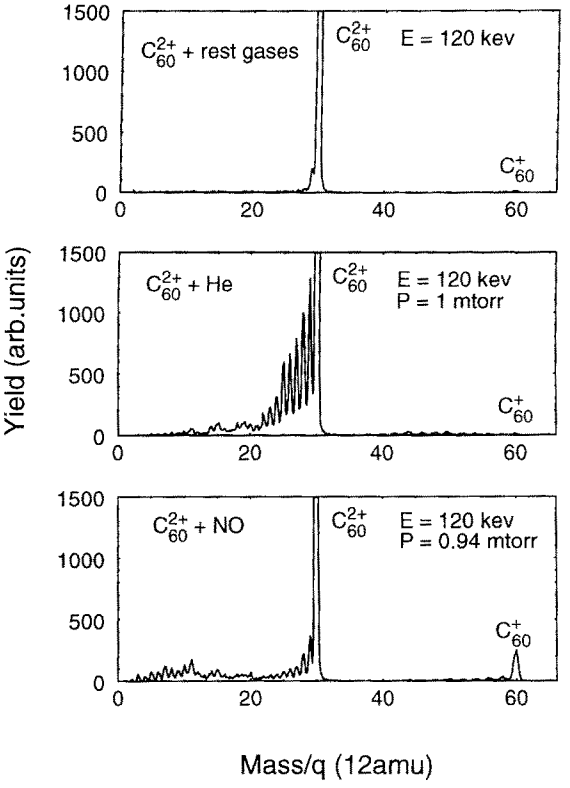

Fig. 2. M/q (mass divided by charge) spectra resulting from interaction of 120 keV C_{60}^{2+} with rest gas (**a**), He (**b**), and NO (**c**)

electrostatically accelerated to energies between 40 and 120 keV. After acceleration, the ions were momentum-selected by a 90° analyzing magnet before entering the 3 cm long gas cell. The ions exiting the gas cell were deflected by an electrostatic analyzer 35 cm downstream from the target and finally counted by a ceratron electron multiplier detector. Spectra as shown in Fig. 2 were obtained by sweeping the analyzer voltage and counting charged C_{60} ions or fragments. In Fig. 2a is shown a spectrum where no gas is admitted to the target cell. The dominant peak corresponds to the primary C_{60}^{2+} ions, and the small peaks result from collisions with rest-gas atoms ($p \approx 10^{-7}$ torr). In Fig. 2b is shown a similar spectrum but now with 1 mtorr He in the target cell. The dominant peaks apart from the primary-ion peak relate to collisionally induced fragmentation of C_{60}^{2+}. Figure 2c shows a spectrum for NO as a target gas, and now electron capture resulting in C_{60}^{+} is found to be an important reaction channel. In the actual cross-section measurements, spectra as shown in Fig. 2 were recorded at various target pressures. The relative intensity of the beam resulting from charge transfer F is then recorded as a function of the target thickness μ. The charge-transfer cross section σ_{ct} is found by plotting the left-hand side of the equation

$$\frac{F(\mu)}{\mu} = \sigma_{ct} - B \cdot \mu \tag{3}$$

and extrapolating to $\mu = 0$ (see Fig. 3). It should be noted that (3), where B is a constant associated with the effect of double collisions, is valid only at low target pressures where the influence of triple collisions is negligible (see, e.g., [13]). The absolute uncertainty of the reported cross sections is $\leqq \pm 20\%$.

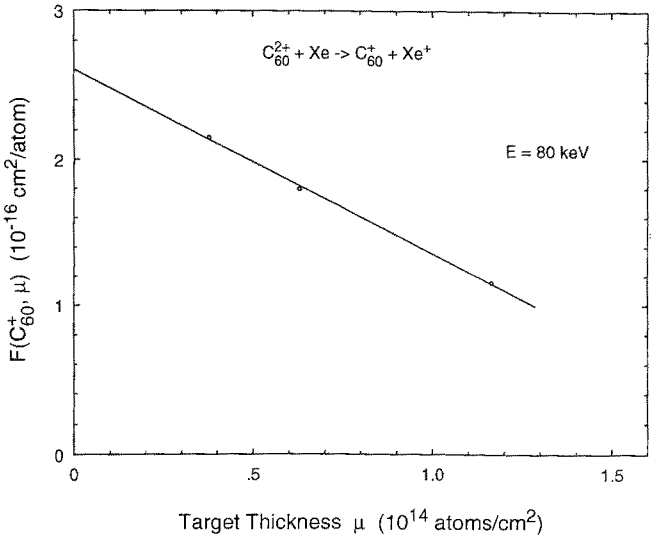

Fig. 3. The relative intensity of C_{60}^{+} divided by target thickness as a function of target thickness for 80 keV C_{60}^{2+} interacting with Xe. The capture cross section is obtained from this plot by extrapolating to $\mu = 0$

3. Results

The measured charge-transfer cross sections for 120 keV C_{60}^{2+} and C_{60}^{3+} are shown in Fig. 4 as a function of target-ionization potential. The lines at 11.8 eV and 15.6 eV indicate the second and third ionization potential of C_{60}, respectively, as reported by Petrie et al. [2]. It is readily observed that the cross sections decrease with increasing target-ionization potential. It should further be noted that the absolute value of the cross section is at most 25% of the geometrical cross section for a C_{60} molecule. The cross-section dependence on the target-ionization potential is similar for the two ions, a finding which at first sight might be surprising, taking the larger projectile-ionization potential of C_{60}^{2+} relative to C_{60}^{+} into account. Note also that the cross section for the most exothermic process (collisions with NO) increases almost with the projectile charge to the second power.

In Fig. 5 is shown the energy dependence for the charge-transfer cross section for C_{60}^{2+} in collision with

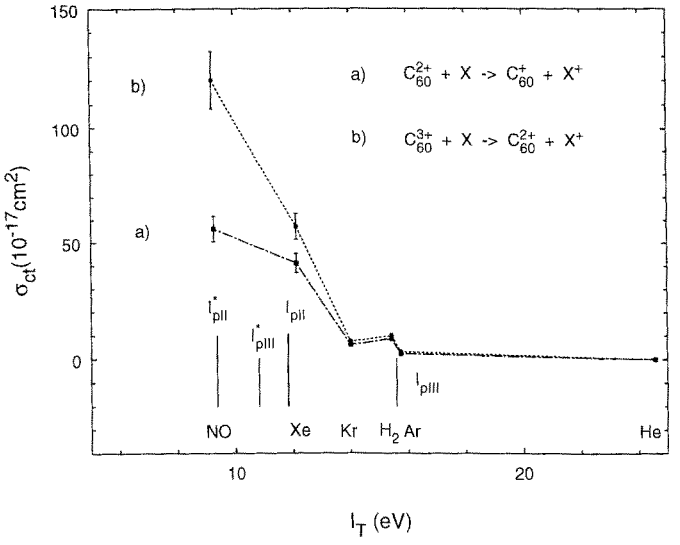

Fig. 4. Charge-transfer cross section as a function of target-ionization potential for 120 keV C_{60}^{2+} and C_{60}^{3+}. The lines indicate the second and third ionization potentials I_{pII} and I_{pIII}, respectively. Also shown are I^*_{pII} and I^*_{pIII}

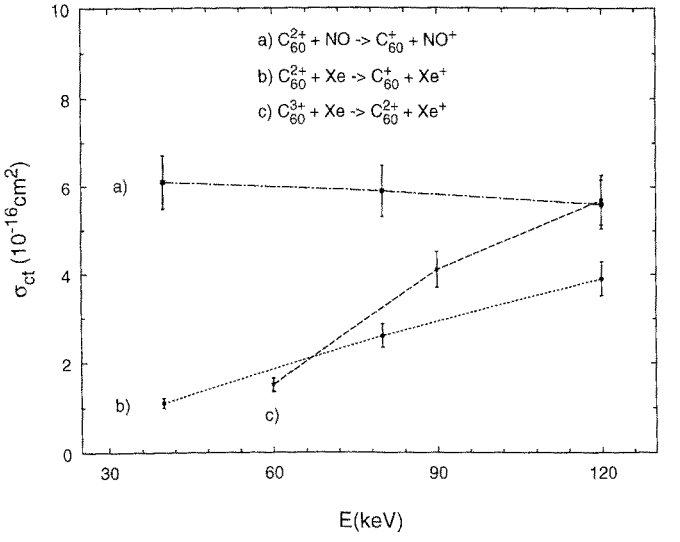

Fig. 5. Charge-transfer cross section as a function of collision energy for C_{60}^{2+} and C_{60}^{3+} interacting with NO and Xe

NO and Xe. As expected, the cross section for charge transfer in NO, which is exothermic, decreases with increasing energy, while the opposite dependence is observed for endothermic charge transfer from Xe. Also shown is the energy dependence of the charge-transfer cross section for C_{60}^{3+} in collisions with Xe. This process is believed to be exothermic, but as seen, the charge-transfer cross section increases with increasing energy – contrary to what might be expected.

4. Discussion

For charge transfer in collisions between multiply charged ions and atoms, which is normally exothermic, a simple over-barrier model has proven to be quite successful [14, 15]. This model states that capture may take place at an internuclear separation where the Stark-shifted initial-energy level of the electron rises above the barrier separating the two ionic cores (see Fig. 6). This situation is met for an internuclear distance (atomic units),

$$R=\frac{1}{I_T}[2\sqrt{q}+1], \tag{4}$$

where I_T is the target-ionization energy and q is the projectile-charge state. However, if at this distance, the Stark-shifted initial-energy level is below the Stark-shifted projectile ground state, capture is exluded. The internuclear distance R_1, at which the energy-resonance condition is fulfilled, is found from

$$I_T+\frac{q}{R_1}=I_p+\frac{1}{R_1}, \tag{5}$$

where I_p is the binding energy of an extra electron on the projectile. The condition for capture to take place can now be formulated as

$$R_1 \leqq R \tag{6}$$

or

$$\frac{I_p}{I_T} \geqq \frac{q-1}{2\sqrt{q}+1}+1. \tag{7}$$

The values of the right-hand side of (7) are listed in Table 1 for various q values.

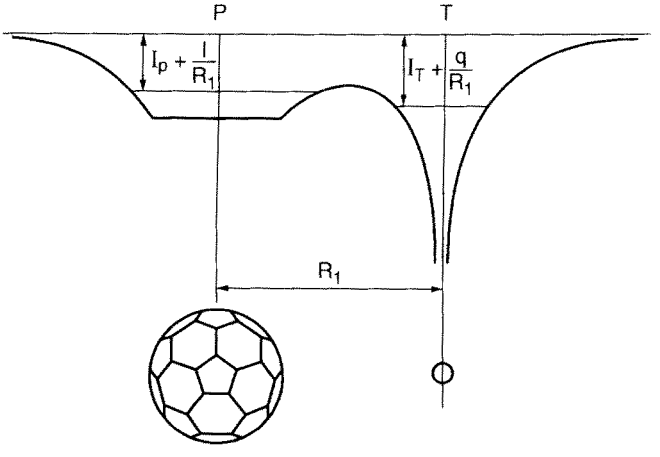

Fig. 6. The classical over-barrier transition model. The projectile (P) is a q times charged C_{60} molecule with ionization potential I_p and the target T is an atom with ionization potential I_T

Table 1

$(q-1)/(2\sqrt{q}+1)+1$	
1	1
2	1.26
3	1.45
4	1.60

Equation (7) readily indicates that the 'bracketing' method can be used only to determine the ionization potential for neutral species I_I which is determined in collisions involving $q=1$ ions. The 'bracketing' method is built on the assumption that charge transfer at low energies can take place only when $I_T \leqq I_p$. In order for a doubly charged ion to capture an electron from a neutral particle, $I_p(=I_{II})$ has to be 26% larger than the target-ionization potential. For $I_p(=I_{III})$, this value is 45%, etc. In general, charge transfer can only take place at low energies when $I_T \leqq I_p^*$ where

$$I_p^* = I_p \left/ \left[\frac{q-1}{2\sqrt{q+1}} + 1 \right] \right. . \tag{8}$$

With the values $I_{II}=11.8$ eV and $I_{III}=15.6$ eV, we find that low-energy capture will take place in gases with $I_T \leqq 9.37$ for C_{60}^{2+} and with $I_T \leqq 10.75$ eV for C_{60}^{3+}.

Figure 5 shows that C_{60}^{2+} can capture an electron from NO at low energies, while neither C_{60}^{2+} nor C_{60}^{3+} can capture from Xe. This can readily be understood on the basis of this simple model. In Table 2, the 'Energy shifts' $(ES)=I_p-I_p^*$ are compared with those of [8], and surprisingly good agreement is obtained, taking the simplicity of our approach into account.

At higher velocities, the so-called intermediate-velocity region capture may still proceed even in the case where the electron is bound more strongly in the target than on the projectile ion. The capture cross section normally attains its maximum value when

$$a|\Delta E|/\hbar v \approx 1, \tag{9}$$

a condition which is in accord with the qualitative 'near-adiabatic' theory proposed by Massey [16]. Here a is a typical transfer distance, v is the projectile velocity, and ΔE is the energy defect in the collision.

It is interesting to note from Fig. 7 that the dependence on the energy defect of the reaction is in qualitative

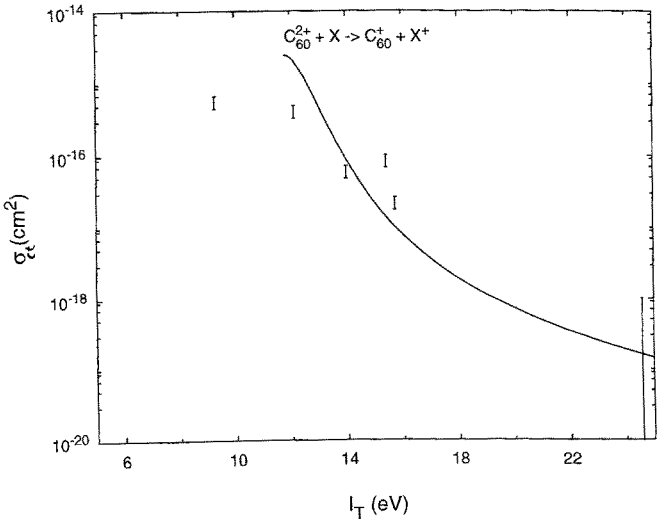

Fig. 7. The same experimental results as in Fig. 4 for C_{60}^{2+} but now compared with theoretical results based on the Rapp and Francis theory [11]

Table 2

q	I (eV)	ES (eV)[a]	ES (eV) present
1	7.6	0	0
2	11.8	2.06	2.43
3	15.6	4.51	4.84
4	19.5	7.1	7.3

accord with the model of Rapp and Francis [11] derived in a two-state model of electron transfer in ion-atom collisions. Apparently, electron transfer takes place in collisions where the target remains outside the C_{60} molecule, and thus elements of simple ion-atom – collision theory can be applied also in collisions between C_{60} ions and atoms.

5. Conclusion

Charge transfer in collisions between energetic multiply charged C_{60} ions and static gases has been investigated. Both the absolute value of the charge-transfer cross section and its energy dependence are found to depend strongly on the target-ionization potential. The results are explained in a qualitative way by a simple over-barrier model and a simple two-state model. It might be surprising that models derived for collisions between atomic ions and atoms work so well for collisions between multiply charged C_{60} ions and gas targets.

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