Dynamics of the Penning Ionization of Fullerene Molecules by Metastable Neon Atoms

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The collision energy dependence of the cross section for the Penning ionization of C_{60} molecules by metastable neon atoms has been measured in the 0.035−0.5 eV range in a crossed beam experiment. The results show a decreasing trend (∼20%) in the low-energy range up to 0.06 eV, with a slightly increasing dependence in the higher energy range. This behavior is interpreted in terms of the characteristics of the intermolecular interaction: an electron transfer can be possible from the metastable rare gas atom to the C_{60} molecule with the formation of an ion-pair collision complex. At low collision energy the system evolves mainly adiabatically and the ionization occurs mainly from the ion-pair complex. However, at higher collision energies, nonadiabatic transitions become possible and the systems can remain partially "trapped" within the higher adiabatic state with a consequent increase of the ionization probability.

Introduction

The Penning ionization of C_{60} molecules in thermal energy collisions with metastable rare gas atoms has been the subject of recent works. In a flow tube experiment, Jahavery et al.[1] demonstrated that Penning ionization of C_{60} molecules by all metastable rare gas atoms effectively occurs. More recently, two parallel and independent works, one performed in Kaiserslautern by Weber et al.[2] and one in our laboratory by Brunetti et al.,[3] have studied this process in a crossed beam configuration. Both studies led to the same conclusions: the only ionic product is C_{60}^+ and the ionization efficiency decreases on going from metastable helium to metastable xenon atoms. The Kaiserslautern group based their interpretation on a two-step model which involved electronic energy transfer from the metastable rare gas atom to the C_{60} molecule in the first step and competing autoionization and electron−phonon coupling processes in the excited fullerene molecule in the second step.[2] The Perugia group explained the same observations by the properties of the potential energy curves, which describe the interaction between the two neutral collision partners. In particular, it was shown that in the entrance channel, an electron transfer can be possible from the metastable rare gas atom to the C_{60} molecule with the consequent formation of an ion-pair collision complex, characterized by a short atom−molecule distance and therefore high ionization probability. The formation of such a complex, while highly possible for helium and neon, appears to be less probable for heavier rare gases.[3]

The dependence of the ionization cross sections on the collision velocity can provide some additional information which can be useful for a better understanding of the possible role of the ion-pair collision complex. However, this experiment is rather difficult to carry out mainly because of the low intensity of the ion signal, essentially due to the low concentration of molecules in a thermal C_{60} beam. Nevertheless, we have performed this measurement for the Ne*−C_{60} system; it is expected to be the most important one when the ion-pair mechanism is considered. In fact, this system, when compared with those with other metastable rare gas atoms, shows the strongest coupling between the neutral and the ion-pair potential energy surfaces.[3]

In the present paper, we report on a crossed beam measurement of the collision energy dependence of the ionization cross section of C_{60} molecules by metastable neon atoms in the 0.035−0.5 eV range. The results are discussed in terms of the interaction potential energy curves of the two partners. It is found that, at low collision energies, the ionization mainly occurs from the lowest adiabatic state, while, when the energy is increased, the ionization also occurs from the higher adiabatic state. This state is suggested to work as a "trap" for the system, producing an enhancement of the ionization probability.

Experimental Section

The crossed beam apparatus used for the measurements of the present work has been already described in detail.[3,4] Basically, it consists of a metastable rare gas atom beam, which crosses at right angles an effusive secondary beam of fullerene molecules produced by an oven source. The ions produced in the collision zone are extracted, focused, mass analyzed by a quadrupole filter, and then detected by a channel electron multiplier.

The neon beam is produced by a standard effusive source at room temperature coupled with an electron bombardment

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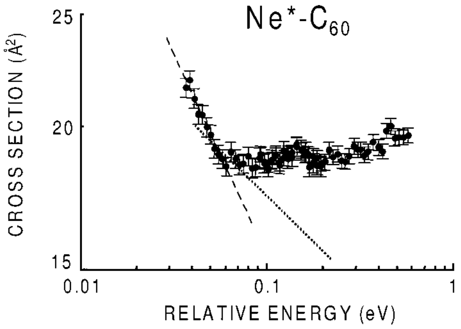

Figure 1. Ionization cross sections for the Ne^*-C_{60} as a function of the collision energy. The relative cross sections measured in the present crossed beam experiment were normalized to the absolute value at 0.086 eV reported by ref 2. The dashed line is the calculation performed by using the ion-pair adiabatic potential, while the dotted line is the calculation performed by assuming a neutral nonadiabatic potential.

device. The bombardment is expected to yield $Ne^*(^3P_2)$ and $Ne^*(^3P_0)$ in a population close to the statistical ratio 5:1. The secondary beam of C_{60} molecules is prepared by effusion from an oven at ~650 °C. The metastable atom beam is detected by channel electron multiplier placed along the beam direction, after the scattering center. A total ionization detector monitors the secondary beam.

The metastable atom velocity is analyzed by a time-of-flight (TOF) technique: the beam is pulsed by a rotating slotted disk and the metastable atoms are counted, using a multiscaler, as a function of the delay time from the beam opening. By using this technique the velocity dependence of the cross section is obtained. Time delay spectra of the metastable atom arrival at the collision zone are recorded, as well as the time spectra of the product ion intensity, then the relative cross sections, $\sigma(E)$, are obtained for a given delay time, τ, according to the relation

$$\sigma(E) = \frac{N^+(\tau)v^*}{N^*(\tau)v_r} \qquad (1)$$

where N^+ and N^* are the intensities of the product ions and metastable atoms, respectively, v^* is the laboratory velocity of the metastable atoms, and v_r is the relative collision velocity. The time spectra of C_{60}^+ ions are corrected for the delay produced by the ion flight time through the mass filter. In the electron bombardment exciter, where metastable atoms are formed, also many photons are produced which can photoionize the target molecules. However, by the TOF technique the separation of photoions and Penning ions is very easy, the former being detected at practically zero delay time.

In order to test possible effects on the collision energy dependence of cross sections due to different detection efficiencies of metastable atoms with different velocities, the collision energy dependence of the cross section for the Ne^*-Ar system was measured and compared with previous determinations.[5] The effects appeared to be negligeable.

Since the absolute concentration of molecules and metastable atoms in the scattering volume is not well-known, the cross sections so obtained are on a relative scale. However, we have normalized the present results to the absolute value of 18.4×10^{-20} m^2, provided by Weber et al.[2] for the collision energy of 0.086 eV.

Results and Discussion

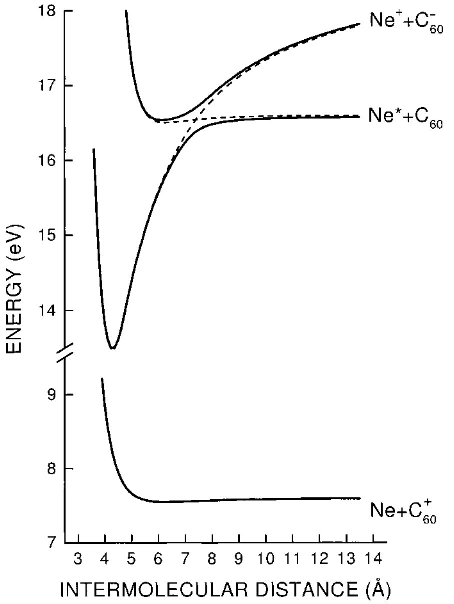

Figure 2. Potential energy curves describing the average interaction between C_{60} molecules and metastable neon atoms. The nonadiabatic curves (dashed lines) were obtained by using some correlation rules (see ref 3). The long-range attraction between C_{60}^- and Ne^+ is connected to the minimum region curve by a cubic spline function. The full line curves are the adiabatic curves obtained by using a coupling of 0.16 eV between the two nonadiabatic curves. In the figure the $Ne-C_{60}^+$ curve, which represents the interaction in the product exit channel, is also reported.

The ionization cross sections for Ne^*-C_{60}, as obtained in the present experiment, are reported in Figure 1 as a function of the collision energy. In the low-energy range (0.02−0.06 eV) the cross sections show a decreasing trend, while they appear to increase slightly in the higher energy range. A change of trend in the collision energy dependence of Penning ionization cross section has been previously observed in some other systems[6−12] and was interpreted[12] as an effect of the passage from a low-energy region, where the attractive branch of the potential is probed, into a region where the cross section is mainly determined by a repulsive potential. To better investigate the effect of the intermolecular potential on the present ionization cross sections, we discuss below the potential energy interaction between a metastable neon atom and a C_{60} molecule.

In a previous work[3] we have estimated the interaction parameters for a C_{60} molecule interacting with a metastable rare gas atom, by using correlation rules based on properties of the separate partners.[13−15] For metastable neon we have found a potential minimum, for the neutral−neutral van der Waals interaction, of 0.095 eV at a distance of 6.28 Å. For the ion pair $Ne^+-C_{60}^-$, the potential minimum was found to be 5.4 eV (with respect to the asymptotic $Ne^+ + C_{60}^-$ energy) at 4.29 Å. For the exit product channel $Ne-C_{60}^+$ the potential minimum was of 0.005 eV at 6.29 Å. These results suggested that a crossing between the ion pair and the van der Waals curve actually exists. Assuming for the long-range ion-pair attraction an induction[3] interaction, in addition to the Coulombic one, the crossing distance has been determined to be 7.3 Å. In Figure 2 the relevant potential energy curves are reported. They have been plotted by assuming the following functional forms: (a) for the van der Waals Ne^*-C_{60} interaction a Lennard-Jones (12,6) potential function has been used (dashed line in the figure); (b) for the ion-pair interaction, a Coulombic plus induction interaction[3] has been used for the long-range attraction, at distances longer than 6.7 Å, while a modified Rittner potential model[14] has been used around the minimum, at distances shorter than 4.8 Å; the two branches have been connected smoothly by a cubic spline (dashed line in the figure); (c) for the Ne$-$C$_{60}$$^+$ interaction a Lennard-Jones (8,4) potential form has been used (full line); (d) the two nonadiabatic potential energy curves, V_1 and V_2, (dashed lines) have been taken into account to calculate the adiabatic curves (full lines) by using the standard formula

$$V_{\text{adiab}} = \frac{V_1 + V_2}{2} \pm \sqrt{\left(\frac{V_1 - V_2}{2}\right)^2 + {V_{12}}^2} \qquad (2)$$

where the coupling term V_{12} has been estimated to be $\sim$0.16 eV by using a simple formula recently proposed.[16] The energy scale in the figure is referred to the energy of the ground state of Ne + C$_{60}$. It is necessary to note that the potential curve representation of Figure 2 is approximate, since it assumes that C$_{60}$, C$_{60}$$^+$, and C$_{60}$$^-$ are simple atomic species without any structure and with a well-defined energy level, while they have obviously a small anisotropy and also many possible internal states. A more realistic representation should take into account also the manifold of states of the neutral or ionic molecular partner. Nevertheless, the curve representation of Figure 2 can be considered appropriate to describe the qualitative features of the Ne*$-$C$_{60}$ collision dynamics as in the following.

From the potential energy curves of Figure 2 one can argue that when the two colliding partners reach the crossing distance, an electron transfer becomes energetically possible. At low collision energy, the dynamics should follow the adiabatic interaction curve, since a nonadiabatic passage to the above curve is very unlike. Therefore, an electron transfer from the metastable atom to the C$_{60}$ molecule can occur and, in such a case, the collision continues on the lowest adiabatic curve. However, the two crossing curves, the one for Ne*$-$C$_{60}$ and the one for Ne$^+$$-C_{60}$$^-$, are always degenerate with the ionization continuum of Ne + C$_{60}$$^+$ + e$^-$ and therefore the system has always the possibility to autoionize ejecting one electron.

When the collision energy increases, at the crossing distance a nonadiabatic passage becomes also possible and, in such a case, the system can evolve partially on the upper adiabatic curve.

We have attempted calculations of the energy dependence of the ionization cross sections by using this very simplified potential energy curve model. We have used a semiclassical approximation[5,17] with an optical potential, that is a complex potential whose imaginary part represents the coupling with the ionization continuum. In a first attempt, we have used simply the lowest adiabatic potential energy curve for the real part, while for the imaginary part an exponential form has been adopted, $\Gamma(R) = a \exp(-bR)$, whose parameters, a and b, have been adjusted tentatively in order to better reproduce the absolute value of cross section. This has been done because, on the basis of our previous experience,[5] we know that the energy dependence of the ionization cross section is mainly affected by the real part of the potential, while the imaginary part mainly determines the size of the cross section. The dashed line in Figure 1 shows the best result obtained. The good agreement between experimental and calculated cross sections, in the low-energy range, is a clear indication that the colliding system behaves adiabatically in this range. The change in the energy dependence for energies higher than $\sim$0.06 eV can be considered an indication that nonadiabatic effects influence the process in the higher collision energy range.

In a second attempt, for energies higher than 0.06 eV, we have tried a calculation by assuming "only" the nonadiabatic potential energy curve for the Ne*$-$C$_{60}$ van der Waals interaction. The results, shown in the figure as a dotted line, lead again to a decreasing trend for the ionization cross sections, although with a different slope when compared with the previous case. The conclusion, which can be drawn from this test, is that the different trend at energies higher than 0.06 eV must be attributed to some effects occurring on the highest adiabatic curve.

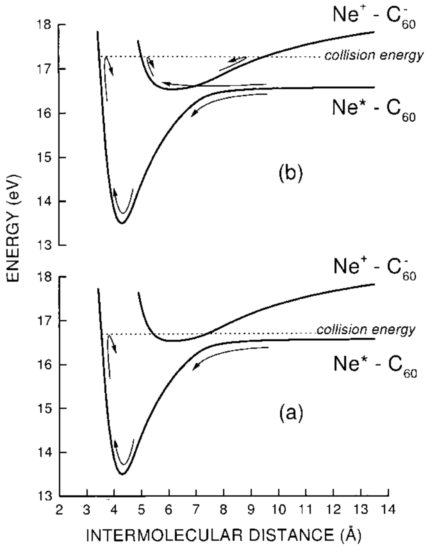

Figure 3. Schematic representation of the Ne*$-$C$_{60}$ collision dynamics at low and high collision energies. (a) At low collision energy the systems behaves essentially adiabatically; that is, the collision evolves mainly along the lower adiabatic potential energy surface. (b) At higher energies, when the system reach the crossing distance, a nonadiabatic transition to the higher adiabatic potential is possible and, in such a case, the system has the possibility to remain partially "trapped" within such a potential well, resulting in an increased ionization probability.

Some years ago Zewail and co-workers[18] studied the dynamical evolution of the NaI system, once excited to the first excited state, by using the femtosecond laser pulse probing technique. The NaI diatom shows a potential energy curve situation very similar to the one of Figure 2: the Na$-$I covalent interaction crosses the ion-pair, Na$^+$$-I^-$, curve at a distance around 7 Å. The first excited state is described by the highest adiabatic curve, which shows a minimum and is rather anharmonic, like the one of Figure 2, but, of course, without the degeneracy with the ionization continuum. Once NaI is pumped to the highest adiabatic state, the system can evolve toward the NaI dissociation, through a nonadiabatic transition to the lowest adiabatic curve, when passing around the crossing distance. The femtosecond probing[18] shows that the systems oscillates several times in the highest adiabatic curve before decaying to the lowest curve, within a time of the order of $\sim$10^{-11} s. This paper is illuminating to understand the collision dynamics in the present system. Here we can also have, during collisions at higher energy, the formation of the excited state, but, in addition to the nonadiabatic decay followed by dissociation, the coupling with the ionization continuum is also present.

In Figure 3 the dynamics of the Ne* + C$_{60}$ Penning ionization, here proposed, has been represented schematically. Scheme (a) illustrates the dynamics at low-energy collision. In this energy range the system behaves adiabatically so that no transition to the above adiabatic potential can occur and, therefore, the collision evolves essentially on the lowest curve. This means that the two partners approach up to the crossing distance ($\sim$7.3 Å) where one electron leaves the metastable atom and is transferred to the fullerene molecule. At this point, the weak van der Waals attraction switches to the stronger Coulombic one and the two ionized partners continue the collision.

Because of the degeneracy with the ionization continuum, along the collision trajectory, autoionization of the system is always possible. The probability for such a process is very high at distances around the turning point. In fact, at such short distances the imaginary part of the optical potential has the highest value and, consequently, the lifetime against the ionization is the shortest. Moreover, the relative velocity of the two colliding partners becomes the slowest one. Scheme (b) illustrates the dynamics in the higher energy range. Here, when the two collision partners reach the crossing distance, the transition probability is not negligible and the system can "partially" pass to the upper adiabatic state. As for the NaI case, in such an excited state the system can remain "trapped", oscillating several times before escaping through a downward transition. Moreover, it is reasonable to imagine that, once in the "trap", the system has the tendency to exchange energy from translation to internal modes of fullerene. This produces a slowing down of the "trapped" system, which further decreases the escaping probability through a downward transition at the crossing distance and consequently increasing the autoionization probability.

The ion-pair model discussed above appears to explain qualitatively the present experimental results. Ion-pair formation was previously invoked to explain the interactions between fullerene molecules and alkali atoms,[19] and these atoms are expected to behave similarly to metastable rare gas atoms.[5] However, the model proposed by Weber et al.[2] could also qualitatively explain the present experimental results: the change in the energy dependence of the cross section around 0.06 eV could be produced by the fact that the contact cross section between C_{60} and the metastable rare gas atom increases toward lower energies due to the influence of the long-range attraction, while it remains almost constant at larger energies where the long-range forces become negligible. In conclusion, the present experimental results do not allow us to assess the reliability of the two possible models which have been suggested for describing the collisional autoionization dynamics, but further experimental and theoretical studies should be necessary to better clarify the dynamics of these processes.

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