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Rapid Communication

Penning ionization of fullerenes: reactions of C_{60} and C_{70} with metastable atoms of the rare gases He, Ne, Ar and Kr

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Abstract

Results of flow-tube experiments are reported for reactions of metastable He, Ne, Ar and Kr with C_{60} and C_{70} at 294 ± 2 K in helium gas at 0.35 Torr. All eight of these reactions were observed to lead to (Penning) chemi-ionization.

Key words: Fullerenes; Metastable atoms; Penning ionization; Chemical-ionization; Flowing afterglow.

Introduction

It is now well established that the novel fullerene molecules can be readily ionized by conventional physical (e.g. electron or photon impact) and chemical ionization (e.g. charge transfer) methods. Double ionization has also been achieved, not only with more conventional electron impact, but also by single-proton ionization using synchrotron radiation [1] and by unprecedented charge-transfer electron-detachment reactions at thermal energies with noble gas ions [2]. Here we report results of flow-tube studies which show that fullerene molecules may also be ionized in thermal-energy chemical reactions with metastable rare-gas atoms in a process, commonly known as Penning ionization, in which electron ejection occurs by the transfer of internal excitation energy from the metastable noble-gas atom to the fullerene molecule.

One of our interests in the reactions of metastable atoms with fullerenes stems from the conjecture that fullerenes are formed in the envelopes of giant, hydrogen-deficient stars such as R Corona Borealis (R Cor Bor) stars [3,4]. In such high-temperature environments He is the dominant gaseous species and metastable helium is likely to be present owing to the abundance of exciting radiation close to the stellar photosphere. Consequently, Penning ionization may compete with other mechanisms of ionization (e.g. photoionization, thermal ionization or charge transfer from He^+) in determining the charge-state distribution of fullerenes in these environments.

From an applications point-of-view, Penning ionization of C_{60} may play a role in the fast-atom bombardment ionization of these molecules by high-energy rare-gas atom beams. Very recent gas-phase fast-atom bombardment experiments reported in this journal using He, Ar and Xe beams to ionize C_{60} implicated Penning ionization by metastable atoms of these rare gases as a contributor to the ionization of C_{60}, although no direct experimental evidence for its occurrence was obtained [5]. The results reported here provide credence for the proposal that the Penning ion-

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ization of C_{60} by metastable rare-gas atoms is possible in such experiments.

Experimental

The experiments were performed with the selected-ion flow tube (SIFT) apparatus which has been described previously [6]. The metastable rare-gas atoms of He, Ne, Ar and Kr were produced in a microwave discharge source (powered by a Raytheon microwave power generator) which we have used previously for hydrogen-atom generation [7]. The cavity was positioned so as to minimize the direct ion signal detected downstream (due to rare-gas ions produced in the discharge) while optimizing the yield of metastable rare-gas atoms (gauged by observing the product ion signals from Penning ionization of N_2 and C_6H_6). The metastable atoms could not be state selected but superelastic collisions with slow electrons convert the $He(^1S_0)$ to $He(^3S_0)$ [8]; the other rare-gas species have resonant (radiative) states in close proximity to the metastable states, and for these species collisions with slow electrons depopulate the upper $^3P_0$ metastable state [8,9]. Bimolecular and termolecular collisions with rare-gas atoms, diffusion, and photoexcitation also serve to depopulate the metastable states.

The fullerene vapour or benzene vapour was added into the flow tube upstream of the inlet of the discharge. It was not possible to measure the amount of the added fullerene vapour quantitatively because of the low vapour pressure of fullerenes. Product ions were monitored with the downstream quadrupole mass filter detection system. The fullerene sample was obtained from Strem Chemicals Co. and was a mixture of C_{60} and 2–12% C_{70}.

All the measurements were performed at 294 ± 2 K in helium buffer gas at a pressure of 0.35 ± 0.01 Torr.

Results and discussion

The Penning ionization of the molecules C_{60}, C_{70} and C_6H_6 was investigated in this study: C_6H_6 was included as a reference compound. For these molecules Penning ionization is energetically possible with He, Ne, Ar and Kr because the metastable levels of these rare-gas atoms all lie above the ionization energies of these molecules. The ionization energies of C_{60}, C_{70} and C_6H_6 are 7.64 ± 0.02 [10], 7.47 ± 0.03 eV [11] and 9.2459 ± 0.0002 eV [12], respectively. The metastable atom energies are as follows: $He^*(^1S_0, {}^3S_1) = 20.6$ and 19.8 eV, $Ne^*(^3P_0, {}^3P_2) = 16.7$ and 16.6 eV, $Ar^*(^3P_0, {}^3P_2) = 11.7$ and 11.6 eV, and $Kr^*(^3P_0, {}^3P_2) = 10.6$ and 9.9 eV [13,14]. With helium there is also the interesting possibility of removing two electrons from C_{60} (and C_{70}) since the metastable levels of this atom also exceed the second ionization energy of C_{60} (and presumably also of C_{70}). Single-photon ionization experiments using synchroton radiation have established a value of 19.00 ± 0.03 eV for the appearance energy of C_{60}^{2+} [1]. Figure 1 provides an energy diagram for the possible reactions of C_{60} with the rare-gas metastable atoms produced in our experiments.

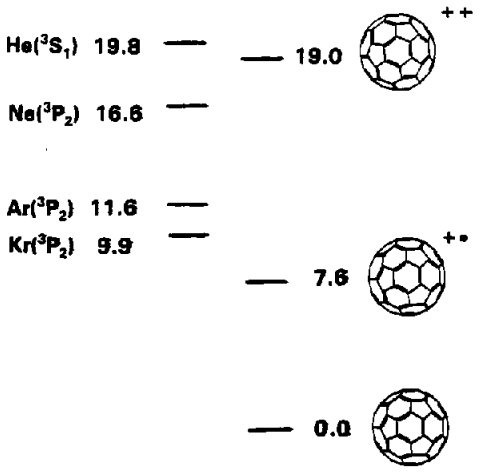

Fig. 1. Energy diagram for the possible reactions of C_{60} with the rare-gas metastable atoms produced in the experiments reported in this study. All energies are in electron volts.

All 12 of the energetically-allowed Penning-ionization reactions were observed in this study. None have been reported previously, including the four Penning-ionization reactions with benzene. Also, it is interesting to note that there was

no evidence for the energetically-allowed double ionization of C_{60} and C_{70} with helium metastables as was the case in our previous studies of the reactions of C_{60} with He^+ and Ne^+ reactions with C_{60} [2]. The Penning-ionization reactions with C_{70} were more difficult to establish because of the possible occurrence of the charge-transfer reaction (1):

$$C_{60}^{\cdot+} + C_{70} \rightarrow CC_{70}^{\cdot+} + C_{60} \quad (1)$$

However, the concentration of C_{70} was considered to be too low for the secondary reaction (1) to contribute significantly to the production of $C_{70}^{\cdot+}$ in the reaction region. The ratio observed for the production of $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$, $C_{60}^{\cdot+}/C_{70}^{\cdot+}$, was found to be equal to the concentration ratio, C_{60}/C_{70}, in the fullerene sample being used in all four metastable reactions.

The Penning ionization process $X^* + Y \rightarrow X + Y^+ + e$, where X^* is the metastable species, is generally understood in terms of the formation of an excited quasi-molecule $(XY)^*$ which undergoes autoionization to produce the final state $X + Y^* + e$. The overall cross-section for Penning ionization is determined by the full interaction potential of the quasi-molecule and also the transition probability for autoionization. In principle these can be calculated quantum mechanically, but this has not been done for the quasi-molecules $(XC_{60})^*$, $(XC_{70})^*$ and $(XC_6H_6)^*$, where X is a noble-gas atom, formed as intermediates in the Penning-ionization reactions investigated in this study.

The inability to monitor the fullerene vapours quantitatively prevented an absolute determination of the rate coefficients for their Penning ionization reactions. However, Penning ionization reactions of helium metastables with polyatomic molecules, including hydrocarbon molecules, are invariably fast, $k \geqslant 1 \times 10^{-10}\,mol^{-1}\,s^{-1}$, at room temperature [15] so that we can expect a similar rate coefficient with the fullerenes.

Our observation of the Penning ionization of C_{60} and C_{70} by helium metastables has a bearing on the production of their ions in stellar envelopes. Penning ionization must be included as a source of ionization in these environments. Also, it renders plausible the suggestion that metastable atoms may contribute to the ionization of fullerenes by fast-atom bombardment [5].

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