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Ionizing reaction cross sections in the collision of argon atoms in high Rydberg states with various molecules

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Measurements of absolute ionizing reaction cross sections in collisions between argon atoms in high Rydberg states (HR) and CCl₄, CCl₃F, CH₃I, SF₆, C₆F₆, CF₄, and CO are reported together with their dependence on the HR argon velocity (570–2100 m/sec). The identity of the positively and negatively charged reaction products has been investigated with a coincidence TOF mass spectrometer. A comparison of the present data with results of other bound and free electron experiments and theoretical predictions is given.

I. INTRODUCTION

The existence of long-lived highly excited Rydberg states (HR) of noble gases was experimentally demonstrated in 1964 by Cermak and Herman.¹ For sufficiently large principal quantum numbers n, such atoms are expected to be nearly hydrogenic in character, since to a good approximation, the excited electron moves in a distant orbit in a near-Coulombic field of essentially unit charge. It is therefore permissible to use the Bohr theory of the hydrogen atom to describe some of their characteristics. High Rydberg atoms are very large in size (mean radius is approximately 500 Å for n = 30). The excited electron is very weakly bound (some meV). Therefore, ionization of HR atoms with n larger than a critical value n_c can occur when passing through a given electric field F_c .²⁻⁷ Field ionization can be used not only to detect but also to discriminate between Rydberg states with different values of n. An important characteristic for collisional studies is their long radiative lifetime ($\tau \sim n^{4.5}$ averaged over all *l* substates) which increases with n and the orbital angular momentum l.^{8,9}

Collsions of highly excited rare gas atoms A (HR) at thermal energy with various molecules (XY) have been investigated in a number of laboratories. Ionization is one of the most important channels. Depending on the nature of the molecule one of several ionizing processes may occur (the charged products formed in the process are given in parentheses): Penning $(XY^+ + e^-)$, rearrangement $(AX^{+} + e^{-})$, and associative $(AXY^{+} + e^{-})$ ionization¹⁰⁻¹² when $XY = H_2$, HD; Penning ionization with fragmentation $(C_2H_3^* + e^-, C_2H_2^* + e^-)$ when XY = $C_2H_4^{1,10}$; ionization of the HR atom $(A^+ + e^-)$ in collisions with polar and quadrupolar molecules like H₂O, SO₂, NH₃, C₂H₅OH, N₂, CH₃NO₂, HCl, HF, etc.¹³⁻²²; dissociative $(A^{+} + X^{-})^{14, 18, 23-26}$ and nondissociative $(A^{+} + XY^{-})^{13, 18, 21, 26-29}$ electron attachment when XY is a molecule which has a large thermal electron attachment cross section.

The collisional ionization of HR atoms with neutral molecules has been treated theoretically by Flannery³⁰ and Matsuzawa.³¹⁻³⁴ Central to their model is the assumption that, because of the large separation between the Rydberg electron and the ionic core, the interaction of this excited electron and the target greatly exceeds that of the ionic core with the target, which can be ignored.

Therefore, the collision of highly excited atoms with a molecule could be regarded as a collision of the Rydberg electron of the excited atom and the target molecule. In the case of polar and quadrupolar targets Matsuzawa^{31, 32} assumes that the Rydberg electron is ionized as a result of its energy gain from the rotational de-excitation of the molecule XY. When the target is a molecule with high efficiency for thermal electron attachment, the rate constant for the HR-atom ionization has been assumed to be equal to that of the nondissociative³³ or dissociative³⁴ thermal electron capture by the molecule XY.

On the other hand, some attempts have been made to describe the collision between the HR atom and the molecule as occurring between two atomic systems. Hotop and Niehaus¹¹ have studied the reaction Ar (HR) + HD and explained the rearrangement ionization process in terms of a crossing of the potential curves of the two systems [Ar (HR) + HD] and $[Ar^{*} + HD]$. The present authors²⁵ proposed a model for the reaction Ar (HR) + CCl₄, CCl₃F where the dissociative electron attachment process is supposed to proceed via the "orbiting-controlled" ioniccovalent curve crossing mechanism.

In the present paper absolute cross sections for the ionizing reactions in the collision of HR argon atoms with a number of molecules (CCl₄, CCl₃F, CH₃I, CH₃Br, C₆F₆, SF₆, CF₄, and CO) have been measured for the first time as a function of the HR argon velocity. Such data are very useful for further investigations on reaction dynamics.

Argon atoms in highly excited Rydberg states have been produced by electron impact. The charged products of the reactions have been analyzed using a coincidence time-of-flight mass spectrometer. Its main advantage is the possibility of measuring simultaneously all ionizing channels of the collision and of identifying the two charged collision products of every process.

II. APPARATUS AND PROCEDURE

In the present experiment absolute ionizing reaction cross sections have been determined by using the apparatus shown in Fig. 1 and relative reaction cross sections have been obtained with a modified form of the apparatus (Fig. 2).

A beam of ground state argon atoms obtained with a supersonic molecular beam generator is excited by a magnetically confined electron beam. After elimination of the charged particles and because of the deviation of



FIG. 1. Schematic diagram of the apparatus in the collision chamber experiment for the measurements of absolute cross sections.

the excited jet with respect to the neutral beam axis, only tains an est electrically neutral, long-lived excited species (metastables and HR) are allowed to reach the interaction zone. multiplier. In the first version of the apparatus (Fig. 1) the HR argon beam passes through a collision chamber which con-In the sec

tains an essentially static gas XY and the positive reaction products are collected directly on a particle multiplier.

In the second version of the apparatus, the beam inter-



FIG. 2. Schematic diagram of the apparatus in the crossed beam experiment with mass analysis of the ionized products of the reaction.

sects at right angles an effusive jet of target molecules XY and the charged products are mass analyzed in a coincidence time-of-flight mass spectrometer (CTOF). Such an analysis enables one to determine the various reaction paths and the relative contribution of each process to the total ionization cross section. For all the molecules XY reported in the present paper only one principal ionizing output channel has been observed (cross section of a 2 to 3 order of magnitude larger than the others).

Certain important aspects of the experimental technique will now be discussed in more detail followed by a description of the procedure for determination of the various cross sections.

A. Supersonic beam generator

The supersonic beam generator which is used in the present experiment (Fig. 1) was conceived by Campargue³⁵ and built by Nenner *et al.*^{36, 37}

It consists of three chambers which are connected by diaphragms (nozzle, skimmer, and collimator) and pumped separately in order to obtain decreasing pressures in the chambers $(p_1 > p_2 > p_3)$. The classical effusion through a circular hole is thus replaced by the well-ordered movement of a Laval jet and only the axial part of the beam is extracted and transferred in the following chamber.

The intensity of the beam depends on the geometry of the diaphragms and their respective distances, the residual pressure P_1 and P_2 , and on the source gas pressure P_0 . The invasion of the free jet by the residual gas molecules has been substantially decreased by increasing P_0 . As a result of these working conditions not only a high intensity has been obtained (10¹⁸ part/sr/sec of Ar at 298 °K) but a decrease in the required pumping speed and thus in the size of the generator was achieved.

The argon atoms' velocity distribution in the beam is measured by a simple time-of-flight technique using a pulsed excitation electron beam and detecting the metastable atoms after a 50 cm flight path. The velocity spread is $\Delta v/v \leq 10\%$ so that for our purposes the beam could be considered as monochromatic. The divergence of the beam (2 β) is equal to 12 mrad.

B. Excitation and composition of the beam

The HR argon atoms are produced by collision of ground state argon atoms with electrons. The electron beam is produced by a classical electron gun with a tungsten filament and two extraction plates with slits parallel to the Ar beam. The excitation takes place in a field free region (between two electrodes at the same potential). A magnetic field confines the electrons in the gun. A typical electron current of 200 μ A at an electron energy of about 40 eV was used in the present experiment. As a consequence, ionization and excitation to states other than the high Rydberg also occur. Elimination of charged particles from the beam was accomplished by the magnetic and electric field in the gun.

The entrance to the collision chamber (or the CTOF

mass spectrometer) is located 6 cm downstream from the electron gun, and only long-lived excited argon atoms (metastable and HR) can reach the interaction zone.

In the course of excitation, the atoms are deviated from their original trajectory. The magnitude of deviation is inversely proportional to the mass and velocity of the species for similar momentum transfer of the electron.^{36, 38} Thus the long-lived excited Ar and H₂ (in the case of the seeded beam) are well separated because the deviation angles are very different. To check this, a pure H, beam has been excited and no signal has been detected on the electron multiplier. For the same reason and because of the small divergence of the neutral beam, very few of the ground state Ar and H₂ will enter the interaction zone. Argon resonance radiation and other UV photons are also produced in the excitation region. The contribution of these photons together with the contribution of the metastable argon atoms to the measured ion intensities will be discussed in Sec. IIF.

The observed HR atoms belong to series converging to the first ionization limit ${}^{2}P_{3/2}$ and have *n* values in the range 15-60 and probably high *l* values.²⁵ Among the excited states belonging to series converging to ${}^{2}P_{1/2}$ those lying between the two ionization limits decay by autoionization within ~10⁻¹³ sec, while those lying below the ${}^{2}P_{3/2}$ limit have low *n* values and decay in flight by fluorescence.

C. Collision chamber

The collision chamber is a cylinder (14 mm i.d.) limited by two plates (Fig. 1). Two circular electrodes $(\phi \ 12 \text{ mm})$ are placed symmetrically with respect to the beam axis 5 mm apart and are used to extract the ions from the interaction zone. The inlet (ϕ 0.3 mm) and exit $(\phi 0.5 \text{ mm})$ apertures for the HR beam are placed symmetrically with respect to its trajectory, i.e., displaced with respect to the neutral beam axis. The collision chamber is fixed on a tube which can be moved from outside the evacuated experimental chamber. Thus, the position of the inlet aperture can be adjusted to sample the maximum of the intensity distribution. The exit slits for the ions on one of the electrodes and the plate are 1×10 mm in cross section. The ions are accelerated directly into a particle multiplier (R.T.C., 56 P 17/2) placed behind the last slit. The pressure is measured with a capacitance manometer (MKS Baratron 90 M-XR) placed at the other end of the tube. A correction factor taking into account the conductance of the introduction tube and of the collision chamber apertures has been used to determine the number density N_{XY} of the target molecule in the interaction zone.

D. Coincidence time-of-flight mass spectrometer

A coincidence TOF mass spectrometer has been built to identify the ion-pair formation processes contributing to the total ionization yield. A schematic diagram is given in Fig. 2.

When a pair of charged particles is formed in a collision process one of them can be used to indicate the



FIG. 3. Coincidence time-of-flight mass spectrum of the positive reaction products in the collision of HR argon atoms with CCl_4 .

moment of formation, and the time of flight of the second can be used to determine their masses. The interaction region is located in the first chamber of the mass spectrometer between two grids. A weak electric field (about 100 V/cm) extracts the ion pair (or e^- + ion) produced in the collision of the HR argon beam and the effusive jet of target molecules. The target gas is introduced in the interaction region through a 10 mm long capillary tube $(\phi 0.5 \text{ mm})$ which defines the effusive beam. This interaction region is wide open in order to reduce the residual pressure and to prevent collision of metastable atoms with metal surfaces. Depending on the polarity of the electric field, one of the ions (positive or negative) is accelerated toward a channel plate multiplier located at a very short distance from the grid. The signal of this detector starts a time-to-amplitude converter (TAC). The other ion is in the mean time accelerated through an ordinary time-of-flight mass spectrometer.³⁹ This spectrometer has two acceleration regions (6.5 and 10 mm length, respectively) and the fields are applied on circular copper grids (ϕ 14 mm) of 80% transparency. In the first acceleration chamber two grounded circular electrodes with a 10 mm ϕ hole and a tube (0.5 mm i.d. are mounted in order to protect the HR atoms from field ionization before reaching the interaction region. After acceleration the ions travel through a 20 cm long field free region and are then collected on another channel plate multiplier whose signal stops the TAC. This region is screened by two concentric tubes (25 and 50 mm ϕ , respectively) on which the same potential is applied as to the grids which limit the free flight path. Four half electrodes are placed between the tubes in order to be able to correct the ion trajectory and an additional connection to the pumping system of the experimental chamber ensures a vacuum better than 10⁻⁶ Torr. The whole mass spectrometer is mounted in a grounded envelope which can be moved from outside in order to perform the extremely fine alignment of the entrance aperture with the supersonic beam.

The working conditions are chosen in order to satisfy the time-focusing conditions of Wiley and McLaren.³⁹ The total energy of the ions is ~600 eV and the overall resolution obtained is about 50. A typical time of flight of $Ar^*(+e^-)$ is about 5 μ sec but the band path of the whole counting system (TAC + multichannel analyzer) is of the order of 40 kHz.

As only ~50-100 coincidence per sec have been mea-

sured in the present study, no possibility exists that some coincidences escape detection because of counting system "dead time."

A typical coincidence time-of-flight mass spectrum of the positive species obtained in the collision of HR argon atoms and CCl₄ is shown in Fig. 3. Every peak of this spectrum corresponds to a different output channel of the collision. The starts of the TAC are given by the respective negative species. Electrons will have a flight time of a few nsec between the point of formation and the detector, while the negative ions will reach the detector within $\approx 1 \ \mu$ sec. Therefore, a positive ion (Ar^{*}, for example) formed in coincidence with a negative ion (Cl⁻, for example) will appear about 1 μ sec earlier in the TOF spectrum than the same ion produced in coincidence with an e^* .

The dissociative electron attachment of CCl_4 gives rise to the peak at ~4 μ sec and is the principal channel of the collision:

$$Ar(HR) + CCl_4 - Ar^* + Cl^- + CCl_3 . \tag{1}$$

The ionization of HR argon in the electric field present in the interaction region and by blackbody radiation^{40, 41} gives the couple $Ar^* + e^-$ and the peak is located at 5 μ sec, although the flight time of the same positive ion has been measured. This peak does not arise by autodetachment of CCl₄ before dissociation into Cl⁻ + CCl₃ or collisional ionization of HR argon atoms by CCl₄.

The collisional ionization of HR argon atoms in the reaction

$$Ar(HR) + M - Ar^{*} + M + e^{-}, \qquad (2)$$

where M is a polar molecule such as H_2O which is always present in the residual gas contributes also to the peak at 5 μ sec.

The Penning ionization of the target molecule and of the residual gas (H₂O) resulting from the collision with both HR and ${}^{3}P_{0,2}$ metastable argon atoms gives rise to the peak at 9.2 μ sec for

$$\operatorname{Ar}(\operatorname{HR}) + \operatorname{CCl}_{4} - \operatorname{Ar} + \operatorname{CCl}_{4}^{*} + e^{-}, \qquad (3)$$

$$\operatorname{Ar}({}^{3}P_{0,2}) + \operatorname{CCl}_{4} - \operatorname{Ar} + \operatorname{CCl}_{4}^{*} + e^{-},$$
 (4)

and at 3.1 μ sec for

$$Ar(HR) + H_2O - Ar + H_2O^* + e^-$$
. (5)

The respective contribution of the reactions (3) and (4) to the peak at 9.2 μ sec can be determined by applying a strong electric field to the *n*-analyzer plates located between the excitation and interaction region, which ionizes nearly all HR atoms before they reach the reaction zone.

E. Determination of the absolute ionizing reaction cross sections

For the collision Ar(HR) + XY with a well defined relative velocity v_{rel} , the attenuation of the flux of HR atoms intensity due to collisions is given by

$$I(x) = I_0 \exp(-\sigma_{\text{tot}} N_{\text{XY}} x) , \qquad (6)$$

where N_{XY} is the number density of the target molecules

and I(x) the flux of HR atoms at position x. The cross section σ_{tot} includes all the reactions which contribute to the disappearance of Ar(HR). The flux of the ionized reaction products is given by

$$I^{+} = I_0 \frac{\sigma_R}{\sigma_{\text{tot}}} \left[1 - \exp(-\sigma_{\text{tot}} N_{\text{XY}} L) \right], \qquad (7)$$

where σ_R is the ionizing reaction cross section and *L* the reaction path length.

The initial intensity of HR atoms has been obtained by measuring I^* as a function of the target gas pressure. The constant level attained by I^* at higher pressure corresponds to the initial intensity I_0 (i.e., all HR atoms have reacted). If we assume that the ionization is the most important process in the collision (i.e., $\sigma_{tot} \approx \sigma_R$), both I_0 and I^* are measured with the same relative uncertainty and the reaction cross section can be determined using the following equation:

$$\sigma_R = \frac{1}{N_{XY}L} \ln \frac{I_0}{I_0 - I^{+or}} .$$
 (8)

This determination thus requires absolute values for N_{XY} and L, but only relative values of I^* and I_0 . We note however, that the cross section for n and l changing can be in some cases²² larger than the ionization cross section. Thus, in fact, the experiment should be conducted at target gas pressure low enough that most of the I^* ion signal results from collisional ionization of the initial population of Rydberg atoms. The maximum pressure used was between $10^{-5}-10^{-4}$ Torr. In this pressure range and because of the small distance to the detector, the collisional loss of ions was negligible.

A subsidiary experiment has been performed to ensure the validity of the I_0 measurements. The decrease of the intensity of HR atoms leaving the collision chamber has been observed as a function of the target pressure. This has been done by ionizing nearly all HR atoms in a strong field applied between an electrode and a multichannel plate detector located symmetrically with respect to the beam axis downstream from the chamber. At target gas pressures for which the constant level has been observed, no Ar^{*} ions have been detected.

It was also important to ensure that the measured ion intensity I^+ originates solely from the collision Ar(HR) +XY and has no contributions due to (i) photoionization, (ii) chemi-ionization of the residual gas by the Ar ${}^{3}P_{0,2}$ metastables, (iii) secondary electron ejection on solid surfaces by the metastable atoms, (iv) field ionization, or (v) other ionization processes which might form ions outside the collision chamber. Photoionization [(i)] is believed to be unimportant because the cross sections for photoionization of the various target molecules are much smaller than the corresponding cross sections reported in this paper. As a confirmation of this, a test was carried out in which the argon beam was excited by a pulsed electron beam and the counting system gated off for an interval about the time of flight of the HR atoms to the interaction zone (30-100 μ sec). No difference in the ion intensity with gate on and off have been observed.

In the determination of I^* the number of ions is measured with and without target gas present in the interac-

tion region. Subtraction of these signals eliminates the ions produced by the processes (ii), (iii), and (iv). In order to distinguish between the ions formed in the collision chamber and outside of it [(v)], an analogous procedure was used. In this case a sufficiently large retarding field is applied on the extracting electrodes, which prevent the ions formed in the collision chamber from reaching the detector. The effect of the Penning ionization of the target gas by the $Ar^{3}P_{0,2}$ metastables [process (4)] is negligible in the case of CCl_4 and CCl_3F . The intensity of the peak corresponding to the latter process has been found to be a few percent of those for the dominant process (1). In the case of the two other molecules CO and CF_4 , for which absolute measurements have been made, Penning ionization by $Ar^{3}P_{0,2}$ is energetically not possible and has not been observed.

F. Determination of relative reaction cross sections

Relative partial cross sections are obtained from the relative peak areas in the TOF mass spectrum after correction for the different detection efficiencies of electrons and negative ions. Absolute values are then obtained by normalization to the total reaction cross section.

In the present study, only one dominant ionizing reaction output channel has been observed and therefore no correction for different detection efficiency was necessary. The absolute values have been estimated by normalization based on only one absolute cross section for all target molecules, the cross section for dissociative attachment σ_{DA} in the collision of Ar(HR) with CCl₄ [process (1) in Sec. IID].

The initial intensity of HR atoms has been measured . by applying a strong field to the grids of the first acceleration region. Almost all HR atoms are ionized and detected on the nearest channel plate multiplier. The n distribution of the HR argon atoms can be obtained by applying, in addition, a monotonically increasing field on the *n*-analyzer plates. The intensity I_0 decreases with increasing field. The probability of ionization $W(\sec^{-1})$ varies rapidly above threshold for a small change in the electric field. According to hydrogenic theory^{5,8} a change of four or five order of magnitude of W corresponds to a lowering of the critical field value F_c by only 15%-20%. In the present experiment the time spend by HR atoms with different velocities in the strong or variable electric field varies only within a factor of 4 and therefore no correction has been introduced in the calculation of n [n=f(F)]. The intensity I^{+or} is obtained by integration of the respective peak in the mass spectrum, obtained in the normal operating conditions of the CTOF mass spectrometer. No overlap with other peaks perturbs these measurements. No significant difference in the value of the cross section has been observed as a function of the ion count rate used $(I^* \text{ or } I^-)$.

In order to test the validity of the normalization, the absolute cross section of CCl_3F , CO, and CF_4 has also been measured and an agreement within $\pm 5\%$ with the respective normalized absolute cross sections has been found.

XY		CCl4	CCl ₃ F	CH ₃ I ^a	SF ₆ ^a	C ₆ F ₆ ^a	CF4	со
Ar(HR+XY)		$Ar^+ + Cl^- + CCl_3$	$Ar^+ + Cl^- + CCl_2F$	$Ar^{+} + I^{-} + CH_3$	$Ar^+ + SF_6^-$	$Ar^{+}+C_{6}F_{6}^{-}$	$\operatorname{Ar} + \operatorname{C} \operatorname{F}_{4}^{*} + e^{-}$	Ar* + CO + e*
$v_{\rm Ar} = 5.7 \times 10^4$								
	σ k	$(2.9\pm0.6)\ 10^{-12}$ $(1.8\pm0.3)\ 10^{-7}$	$(2.3 \pm 0.4) \ 10^{-12}$ $(1.4 \pm 0.3) \ 10^{-7}$	$(5.2 \pm 1) \ 10^{-13}$ $(3.2 \pm 0.6) \ 10^{-8}$	$(1.7 \pm 0.4) \ 10^{-12}$ $(1.1 \pm 0.2) \ 10^{-7}$	$(1.1 \pm 0.2) \ 10^{-12}$ $(6.6 \pm 1.1) \ 10^{-8}$	$(4.7 \pm 0.8) \ 10^{-14}$ $(3 \pm 0.6) \ 10^{-9}$	(1.1 ± 0.2) 10 ⁻¹³ (8.4 ± 1.7) 10 ⁻⁹
$v_{\rm Ar} = 12.7 \times 10$	4							
	σ	$(1, 4 \pm 0, 3) \ 10^{-12}$	$(1.3 \pm 0.3) \ 10^{-12}$		$(1.3 \pm 0.3) \ 10^{-12}$		$(4.7 \pm 0.9) \ 10^{-14}$	
$v_{Ar} = 21 \times 10^4$								
	σ	$(6.5 \pm 1.2) \ 10^{-13}$	$(0.8 \pm 0.2) \ 10^{-12}$		$(0, 8 \pm 0, 2) \ 10^{-12}$		(3.8 ± 0.7) 10 ⁻¹⁴	
Xe (31f ⁻) ^b	k	$(3.1 \pm 0.6) \ 10^{-7}$ c	$(5.9 \pm 1.1) \ 10^{-7c}$	$(3.9 \pm 1.0) \ 10^{-7c}$	(3.8 ± 0.8) 10 ^{-7d}	$(0.3 \pm 0.08) \ 10^{-7d}$		
Ar (HR) ^e	σ				$(1.5 \pm 0.1) \ 10^{-12}$ $(1.7 \pm 0.1) \ 10^{-12}$			
Ar (HR) ^f	k			8.9×10-7				

TABLE I. Absolute reaction cross sections σ (cm²) and rate constants k (cm³/sec) for the collision of Ar (HR) with various molecules at three argon beam velocities v_{Ar} (cm/sec). Comparison with values reported in the literature at thermal energy.

^aAbsolute values obtained by normalization (see Sec. II F).

 $b_n = 31$ for all molecules except for $C_6 F_6$.

^cReference 24.

^dReference 26.

^eReference 13, first value obtained from observation of Ar^* production, and the second of SF_6^* production. ^fReference 14.

III. RESULTS AND DISCUSSION

Absolute cross sections obtained in the present work are given in Table I for the dominant reaction channel in the collision of Ar(HR) atoms with CCl₄, CCl₃F, CF₄, CO, SF₆, C₈F₆, and CH₃I at three velocities of the Ar(HR) beam. Rate constants calculated from the approximate relation $k = \sigma \overline{v}_r$, where \overline{v}_r is the average velocity of the argon beam relative to the target molecule are also shown. The quoted uncertainties were determined from the individual uncertainties of all quantities appearing in Eq. (8). The major uncertainty arises from the number density N_{XY} to which an uncertainty of 10% is assigned. The statistical error in the I^* and I_0 measurements amounts to less than 5% and the uncertainty of L is estimated to be 2%.

It is of interest to compare the present results at nearly thermal Ar(HR) velocity (Table I) with the data for attachment of free electrons to the target molecule. As mentioned in the introduction, the theoretical results of Matsuzawa, ^{33, 34} based on the "essentially free" electron model, predict that the rate constants for the ionization of HR atoms via electron transfer reactions of the type

$$Ar(HR) + XY - Ar^* + X^- + Y, \qquad (9)$$

$$Ar(HR) + XY - Ar^* + XY^-$$
(10)

will be equal to the thermal electron attachment rate constants, i.e.,

$$e^{-}(\epsilon) + XY \to XY^{-}$$
 (11)

$$- X^- + Y , \qquad (12)$$

where the energy ϵ of the free electron is equal to the binding energy E_n of the HR electron.

The present rate constants are averaged over all n

states with binding energies between 6-36 meV (a mean value of 15 meV for the electron energy is estimated) and the free electron data are usually⁴⁴ obtained at a mean electron energy of ~ 38 meV. Therefore, a comparison of the two sets of data are possible after a reasonable extrapolation of the bound electron data. A similar extrapolation is needed when rate constants for different HR rare gas-XY collisions are compared (the binding energy depends on the ionization potential of the rare gas). On the other hand, the quantities being compared are rate constants and depend on the reactants' velocity distribution which is not the same in the case of Rydberg and free electrons and probably depends on the orbital quantum number l of the Rydberg electron. Therefore, differences between the free and bound electron data are not unexpected. We note also that in the present experiment only rate constants larger than about 10^{-12} cm³ sec⁻¹ can be obtained with good accuracy. This corresponds to values of $\sigma \ge 10^{-15} \text{ cm}^2$.

The Ar(HR)-CCl₄, CCl₃F collisions have been considered in detail elsewhere²⁵; only a summary of the discussion of these results will be given below. Dissociative electron attachment is the principal output channel of the collision in agreement with other studies involving rare gas high Rydberg states, ^{18, 23, 24} although the measured rate constants²⁴ for Xe (nf) + XY (XY = CCl₄ and CCl₃F) lie generally a factor of 2 or more higher than the present results. On the other hand, the present rate constants agree well with the rate constants for electron attachment [process (12)] and as for the free electron data, the rate constants for CCl₄ are greater than those for CCl₃F.

The CTOF spectra of CH_3I show, as for CCl_4 and CCl_3F , that the reaction

$$Ar(HR) + CH_3I - Ar^* + I^- + CH_3$$
(13)

takes place, in agreement with Stockdale *et al.*¹⁴ for Ar(HR) + CH₃I and Hildebrandt *et al.*²⁶ for Xe (nf) + CH₃I. The present rate constants are, once more, smaller than the data reported for Xe (nf)²⁶ (Table I). Measurements on the attachment of free electrons to CH₃I^{14, 42, 43} have shown that process (12) takes place. The rate constant obtained by Lee⁴² (2.45×10⁻⁸ cm³ sec⁻¹) is in good agreement with the present results. Both in the present measurements and those of Lee, the values obtained for CCl₄ and CCl₃F are larger than these for CH₃I. No CH₃I⁻ or ArCH₃⁺ ions were detected and no increase of the Ar⁺ intensity due to collisional ionization of high Rydberg argon atoms has been observed.

In the case of CH₃Br neither the negative ion Br⁻ which would be produced by dissociative electron attachment, nor the positive ion Ar⁺ due to collisional ionization of the HR argon atoms (stripping reaction) have been observed. Stockdale *et al.*¹⁴ also were unable to observe Br⁻. It is assumed, therefore, that the rate constants must be smaller than 10⁻¹² cm³ sec⁻¹. The rate constant obtained for CH₃Br colliding with Xe (nf)²⁶ is found to be 10⁻⁸ cm³ sec⁻¹. There is a considerable disagreement in the literature as to the magnitude of the free thermal electron attachment rate constant. The reported values include (in units of cm³ sec⁻¹) 3.3×10^{-9} , ⁴² 1×10^{-9} , ⁴⁴ 7×10^{-12} , ⁴⁵ and 3.6×10^{-12} . ⁴⁶

The dominant reaction channel for SF_6 is the nondissociative electron attachment

$$Ar(HR) + SF_{6} \rightarrow Ar^{+} + SF_{6}^{-}$$
(14)

in agreement with Hotop *et al.*¹³ for $Ar(HR) + SF_6$, Chupka¹⁵ for $Kr(HR) + SF_6$, Klots¹⁶ for $He(HR) + SF_6$, Hiraishi *et al.*²¹ and Astruc *et al.*²⁹ for $Ar(HR) + SF_6$, and West *et al.*²⁸ and Foltz *et al.*²⁴ for Xe (nf) + SF₆. The present results are in close agreement with the cross section of Hotop *et al.*, ¹³ but are a factor of 3 and more smaller than the values for Xe (nf) + SF₆.^{24,26} It is known⁴⁷ that in addition to the nondissociative attachment of thermal electrons to SF₆ [process (14)] dissociative attachment, producing SF₅ also takes place (although with a small probability at room temperature), but the latter ions have not been observed in the present experiment.

There exist a number of studies on the attachment of the free electron to SF_6 .^{46, 48-55} The values for the rate constants are in the range 2.2×10^{-7} to 2.7×10^{-7} cm³ sec⁻¹ and are about a factor of 2 higher than the present results.

The CTOF spectra of C_6F_6 show that, in addition to process (10), autodetachment of the negative ions C_6F_6 also occurs:

Ar (HR) + C₆F₆ - (Ar⁺ · · · C₆F₆) +

$$\begin{cases}
Ar+ + C6F6, (15a) \\
Ar+ + C6F6 + e- (15b)
\end{cases}$$

in agreement with the observation of Hildebrandt *et al.*²⁶ The rate constant for process (15) is found to be a factor of 2 higher than the results for Xe (nf)²⁶ (Table I) and smaller than those reported in free electron experiments: 1.06×10^{-7} cm³ sec^{-1.56} and 1.02×10^{-7} cm³ sec^{-1.57}

In the latter case, however, the rate constants are determined in experiments where stabilization by collision of temporary negative ions is possible and thus all initially formed ions are taken into account. A loss of negative ions by autodetachment is a possible reason for the observed differences between free and bound electron data.

For all molecules discussed till now, the comparison of the present results with the free electron data indicates a difference of a factor of 2 or 3 in the absolute values, but a good agreement in the relative value is found. Because of the correction factor used in the N_{XY} determination a systematic error is not unexpected, although some differences in the comparison with the bound electron data for Xe (nf) remain unexplained.

The CTOF mass spectra of CF_4 indicates that the dominant reaction is the Penning ionization

$$\operatorname{Ar}(\operatorname{HR}) + \operatorname{CF}_{4} \to \operatorname{Ar} + \operatorname{CF}_{4}^{*} + e^{-} .$$
(16)

Contribution to the ion count rate, resulting from the collision of metastable argon atoms with CF₄, is not possible on energetic grounds $(IP_{CF_4} = 14.36 \text{ eV})^{58}$ and has not been observed. No negative ions CF₄ or F^{*} have been detected. Although negative ions CF₄ of small intensity have been reported^{42,59} in free electron measurements, Hickam *et al.*⁶⁰ were unable to detect them. The reported values of the rate constants include 8×10^{-13} (Ref. 42) and $< 3.1 \times 10^{-13}$ cm³ sec⁻¹.⁵⁶

In the case of CO the collisional ionization of the HR argon atom has been observed:

$$Ar(HR) + CO - Ar^{+} + CO + e^{-}.$$
(17)

The measured cross section is consistent with the theoretical predictions of Matsuzawa^{31, 32} for the ionization of highly excited atoms by rotational de-excitation of the target molecule. The collisional ionization of HR atoms has been studied experimentally in the case of Xe (nf) +NH₃, ND₃ and HCl collisions, ^{20, 22} and Kr (HR) +HF and HCl collisions.¹⁹ Although the experimental data follow the trend of the theoretical predictions, ^{31, 32, 61} i.e., steplike structure in the cross section¹⁹ and increase of the rate constant²² with increasing *n*, the quantitative agreement is not satisfactory.²²

The theoretical model of Matsuzawa^{32,33} for the collision of HR atoms with electron attaching targets seems to be a good first approximation to predict the magnitude of the cross sections and the identity of the reaction products.

Figure 4 shows the relative cross sections for the dissociative electron attachment of CCl_4 process (9), the electron attachment to SF_6 process (10), and the Penning ionization of CF_4 process (16) as a function of the relative velocity v_r . The $\log \sigma_R - \log v_r$ plot is linear for processes (9) and (10). The slope is about minus one. This behavior is typical for exothermic reactions,⁶² where the cross section is proportional to the collision time which decrease with increasing velocity. We note, however, that σ_R is a total cross section, averaged over all n values. The velocity dependence of the dissociative electron attachment cross section in the cases of CCl_4





FIG. 4. Relative cross sections for the ion pair formation and Penning ionization in the collision of HR argon atoms with CCl_4 and SF_6 , respectively; CF_4 as a function of the relative velocity v_r .

and CCl_3F has been measured²⁵ for different ranges of principal quantum number. A different behavior, which is expected for reactions with an energy threshold, has been observed for low *n* values.

The velocity dependence mentioned above indicates that the ion core Ar^* would play a role in the outcome of the experiment and the interaction between the high Rydberg rare gas core and the target molecule cannot be neglected.

On the other hand, the measured cross sections are among the largest yet observed for thermal energy neutral-neutral collisions. This fact may not be a simple consequence of the large physical size of the HR atoms but suggests that the electron transfer takes place with a probability nearly unity at large distance between the Ar^{*} core and XY. This process is thus governed by a long-range interaction.

The cross section for Penning ionization [process (16)] as a function of the relative velocity is nearly constant and of the same order of magnitude as those observed with metastable atoms. Theoretical aspects of this reaction involving metastable rare gas atoms (and not HR) have been investigated by several authors^{63, 64} using momentum transfer methods, orbiting theories, and models based on complex potentials. Simple semi-empirical models^{63, 11} are also proposed to explain the

experimental results. These models indicate that the interaction leading to ionization is short ranged.

In the reaction of HR atoms with electron attaching target molecules, the ionization of the highly excited atom at large distance seems to be the most probable process, but when energetically possible (CCl₄, CCl₃F, CF₄, CH₃Br, CH₃I) Penning ionization of the target molecule also has been observed.

In all cases except for CF_4 the exact measurement of the cross section for the Penning ionization by HR atoms is perturbed whether by the fact that other output channels are more probable (CCl_4 , CCl_3F , CH_3I) or because of Penning ionization by the metastable atoms. It is thus possible that a transfer of an electron from the molecule CF_4 to the ion core takes place when they approach at sufficient small distance. The Rydberg electron can ionize by gain of energy from the repulsion between the atom and this last electron.

Further investigation of this process needs increased knowledge about the HR state and improved sensibility of the apparatus.

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