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Reactions of molecular dications: collision energy dependence of integral cross-sections of processes in $CHCl^{2+} + Ar, D_2$ systems from guided beam studies

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Dedicated to Professor Helmut Schwarz on the occasion of his 60th birthday in
appreciation of his manifold contributions to mass spectrometry and ion chemistry.

Abstract

Collision energy dependence of integral cross-sections of charge transfer processes and chemical reactions in the system $CHCl^{2+} + Ar$ and $CHCl^{2+} + D_2$ was investigated in guided beam experiments. Both singly charged reaction products resulting from non-dissociative charge transfer and chemical reactions in these systems could be identified, in the former system $CHCl^+$, Ar^+; CCl^+, ArH^+, in the latter $CHCl^+$, $D_2{}^+$; $CHDCl^+$; CCl^+, $HD_2{}^+$. The identification of ArH^+ and $HD_2{}^+$ helps to specify the reaction of CCl^+ formation as a proton transfer process from the dication $CHCl^{2+}$. The integral cross-section for the charge transfer process with Ar was almost independent of collision energy and its value was close to 2 Å^2; the cross-sections for the chemical reaction of CCl^+ formation with Ar was about 6 Å^2 and showed an increase at low collision energy. The integral cross-section of the reactions with D_2 were of the same order of magnitude as those with Ar.

Keywords: Dications; Integral cross-sections; Charge transfer; Proton transfer

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1. Introduction

Chemical reactions of atomic and molecular dications have attracted considerable attention of both experimentalists and theoreticians in the last years. Earlier reports on reactions of atomic metal dications [1–4] have been augmented by more recent observation of reactions of molecular dications [5]. Later on, isotope effects in molecular dication, hydrogen reactions were studied [6–8], and reactions dynamics of $CF_2{}^{2+}$ [9–11], $CO_2{}^{2+}$ [12], and $CHCl^{2+}$ [13] with hydrogen was investigated in more detail in crossed-beam scattering experiments. Information on integral cross-sections of processes in these systems

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and their dependence on collision energy has been extracted so far from crossed-beam studies in the form of relative cross-sections, proportional to absolute integral cross-sections.

The guided beam method [14–17] represents a direct, reliable approach to measurement of integral cross-sections over a wide range of collision energies, including the low region of laboratory energies below 1 eV. The method was used earlier [15] in measurements of absolute values of the integral cross-section of the $Ar^{2+} + He$ charge transfer reaction and also applied in an ingenious way to estimate absolute values of the differential cross-section of this reaction. Also, recent observation of proton transfer from dications [13,18] often requires unambiguous identification of both singly charged reaction products. This can be achieved in guided beam experiments, while in single beam-collision cell or crossed beam scattering experiments this may create problems. In beam experiments, discrimination in detection of ions with high kinetic energy may occur and in crossed-beam scattering experiments, the light ion product may be scattered backwards in the laboratory frame, inaccessible to measurement. Moreover, a specific method of reactant dication formation, provided in our case by synchrotron radiation ionization, may produce partial state selection of the reactant ion. Integral cross-section data from guided beam experiments usually cannot distinguish contributions to a product from different processes and do not inform on product ion characteristics (translational and/or internal energy, angular distribution). However, they provide an essential information which, in combination with scattering data, complement a detailed picture of reaction kinetics and dynamics of the system.

In this communication, we present results on integral cross-section measurements of reactions in the $CHCl^{2+} + D_2$ and $CHCl^{2+} + Ar$ systems. Reaction dynamics of these systems has been recently studied in crossed beam scattering experiments [13,18] and measurements of integral cross-sections of chemical and charge transfer reactions provide an important piece of information for understanding the kinetics and dynamics of these processes.

2. Experimental

The guided beam apparatus CERISES has been previously described in detail [19,20]. The apparatus consists of three differentially pumped regions: the ion source and reactant-ion quadrupole mass selector, the octopole guided beam section with a reaction chamber, and the product-ion quadrupole mass analyser with the detector.

In the source region, the reactant ions $CHCl^{2+}$ were produced by dissociative double photoionization of the neutral precursor (CH_3Cl) by the synchrotron radiation coming out from a conventional bending-magnet beamline of the SuperACO storage ring.

CERISES has been upgraded to MS/MS capabilities by implementing a quadrupole/octopole/quadrupole arrangement. This configuration permits investigation of both uni-molecular and bimolecular reactions of mass-selected ions. When studying the reactivity of dications, it is mandatory to select a given dication from the ion mixture that emerges from the source: stable dications always appear together with singly charged ionization products and products of dissociative double ionization. After ionization, ions are extracted from the source by a small field of 1 V/cm to assure single-collision regime for reactant dications, and injected through a stack of electrodes into the quadrupole mass filter. At the exit of this filter, the ions are refocused into the first radio frequency octopole guide towards the reaction cell. The reactant ions produced in the source need about 40 μs to reach the end of the first quadrupole filter.

The reaction of the dication takes place within the octopole in a 4-cm long scattering cell filled with the neutral target gas (Ar, D_2) at a typical pressure of 10^{-4} Torr, the absolute value of which can be measured by a Baratron capacitance manometer. The pressure is chosen so to assure a single-collision regime (less than 10% attenuation of the reactant ion beam). The reactant ion kinetic energy is defined by the DC potential on the octopole relative to the potential of the site in the ion source, where ions are formed. It can be varied between 0.6 and 40 eV in the laboratory energy frame, with a typical distribution width of 0.5 eV, full width at half maximum (FWHM). The product ions are confined by the radio frequency guiding field [14,15], then guided by the second octopole, mass selected in the quadrupole mass filter, and finally detected by a multichannel plate detector.

From the measurements of the parent and product ion intensities and the absolute pressure of the neutral target gas, absolute reaction cross-sections can be derived. The absolute integral cross-section σ_{int} can be determined (for $I_\text{P} \ll I_\text{R}$) from $\sigma_{\text{int}} = (I_\text{P}/I_\text{R})(1/n_\text{N}L)$, where I_P is the product ion current, I_R the reactant ion current, n_N the concentration of the neutral reactant in the reaction chamber, and L the collision length in the reaction chamber. In the experiments described here, absolute integral cross-sections were obtained for the reactions with Ar. For the reaction with D_2, because of lack of reliable collision cell pressure calibration for the D_2/H_2 reactant gas, integral cross-sections is presented only in arbitrary units from the ratio of the product ion intensity divided by the reactant dication intensity $\sigma_{\text{int,A}} \sim I_\text{P}/I_\text{R}$. For the same concentration of the neutral reactant in the reaction chamber, n_N, and the same L, these integral cross-sections are directly proportional to the absolute integral cross-sections and they are mutually comparable. In most measurements with singly charged reactant ions, internal energy of a molecular ion is determined by the threshold photoelectron-photoion coincidence (TPEPICO) technique [20,21]. For a full control of the reactant dication internal energy, one would have to use a multiple-coincidence technique [22,23], as four particles are formed in the dissociative double-ionization process employed to produce the reactant ions. This was not possible, because of drastically reduced coincidence intensity. Even the use of a fixed wavelength of the ionizing radiation, as selected by the monochromator, could not be used, as the reactant dication intensity was too low. Instead, a broad band of photon energies was used by setting the monochromator grating to its zeroth order full transmission. This provided at least some selectivity in the wavelength reaching the experiment, which can be described as a broad Gaussian function, with intensity peaking at 40 eV and a FWHM of 20 eV. Thus, no special selection of the electronic state or vibrational energy of the dications was attempted. However, some energy selection is naturally occurring through the lifetime of the produced dication species. Molecular dications are generally metastable species, and highly vibrationally excited species are likely to dissociate over the barrier to two singly charged ions. In our set-up, only non-fragmented ions can emerge from the first quadrupole mass filter. This implies that only species of natural lifetimes long enough (typically longer than 40 μs) to reach the exit of the first quadrupole without fragmentation will be able to react. This puts a certain constraint on the internal energy one can expect to find in the molecular dication.

Neutral gas samples used in the ion source or in the collision cell were all of analytical purity quality, and by recording their mass spectra, the absence of any contaminant before measurements was checked.

3. Results and discussion

3.1. The $CHCl^{2+} + Ar$ system

Fig. 1 shows the mass spectrum of the products resulting from the interaction of $CH^{35}Cl^{2+}$ with Ar in the reaction chamber, at 39.8 eV laboratory energy. The resolution of the first quadrupole was set such that the mass-to-charge ratio of the above mentioned dication (*m*/*z* 24) was well separated from another stable dication occurring in this double ionization system, $CH_2{}^{35}Cl^{2+}$(*m*/*z* 24.5) or of its isotopic analogue $CH^{37}Cl^{2+}$ (*m*/*z* 25). The observed product ions were $CHCl^+$ (*m*/*z* 48), CCl^+ (*m*/*z* 47), ArH^+ (*m*/*z* 41), Ar^+ (*m*/*z* 40), Cl^+ (*m*/*z* 35), and CH^+ (*m*/*z* 13).

From a preceding study of the system in crossed beam scattering experiments at collision energies T of 4.7, 9.0, and 12.6 eV [18], it was concluded—from translational energy and angular measurements of the products $CHCl^+$ and CCl^+—that $CHCl^+$ resulted mainly from non-dissociative charge transfer between the isomer of the $CHCl^{2+}$ dication, $CClH^{2+}$, and Ar (throughout this paper, the formula $CHCl^{n+}$ (with H between C and Cl) is used whenever the isomers

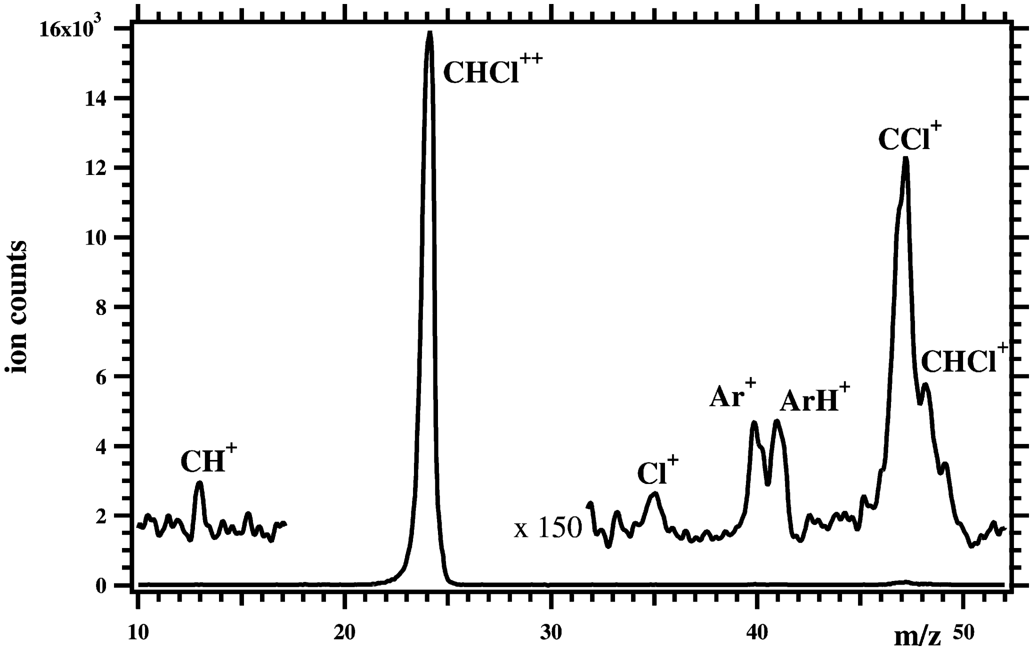

Fig. 1. Mass spectrum of the ion reactant and products from reactions between $CHCl^{2+} + Ar$ at the center-of-mass (c.m.) collision energy of 18 eV.

are not distinguished, and $HCCl^{n+}$ or $CClH^{n+}$ whenever a reference to a particular isomer of the dication ($n = 2$) or cation ($n = 1$) is made).

$$CClH^{2+} + Ar \rightarrow CClH^{+} + Ar^{+} \qquad (1)$$

For the product CCl^{+}, it was inferred that it was mainly formed in a highly exoergic proton transfer process to the neutral target (presumably from both isomers of the dication $CHCl^{2+}$, i.e., both $HCCl^{2+}$ and $CClH^{2+}$)

$$CHCl^{2+} + Ar \rightarrow CCl^{+} + ArH^{+} \qquad (2)$$

In addition, a small amount of CCl^{+} with high internal energy content, originated from further dissociation of a fraction of the charge transfer product of reaction (1)

$$CClH^{+} \rightarrow CCl^{+} + H \qquad (3)$$

The present guided beam experiments fully confirm these conclusions and provide an additional proof by detecting both singly charged reaction products of reactions (1) and (2), $CClH^{+} + Ar^{+}$, and $CCl^{+} + ArH^{+}$, respectively.

Fig. 2 summarizes the data on translational energy dependence of the absolute integral cross-sections $\sigma_{int} = (I_P/I_R)(1/n_N L)$ of formation of the singly charged products originating from reactions (1) and (2). The values of σ_{int} (in Å^2) are plotted here against the collision energy, T. The absolute accuracy of the values is probably not better than about 50%. The dependencies indicate a clear similarity in the behavior of the ion pairs, i.e., CCl^{+} and ArH^{+}, products of reaction (2), and $CHCl^{+}$ and Ar^{+}, products of reaction (1). The scattering experiments [18] showed that the reaction products $CHCl^{+}$ and CCl^{+} were scattered preferentially in the direction of the flight of the reactant dication with translational energies of several eV. This implies that the ion products Ar^{+} and ArH^{+} were scattered preferentially backward with respect to the direction of flight of the reactant dication with high translational energies and that a considerable discrimination in their collection efficiency could occur. This may be the reason why the cross-sections for Ar^{+} and ArH^{+} are

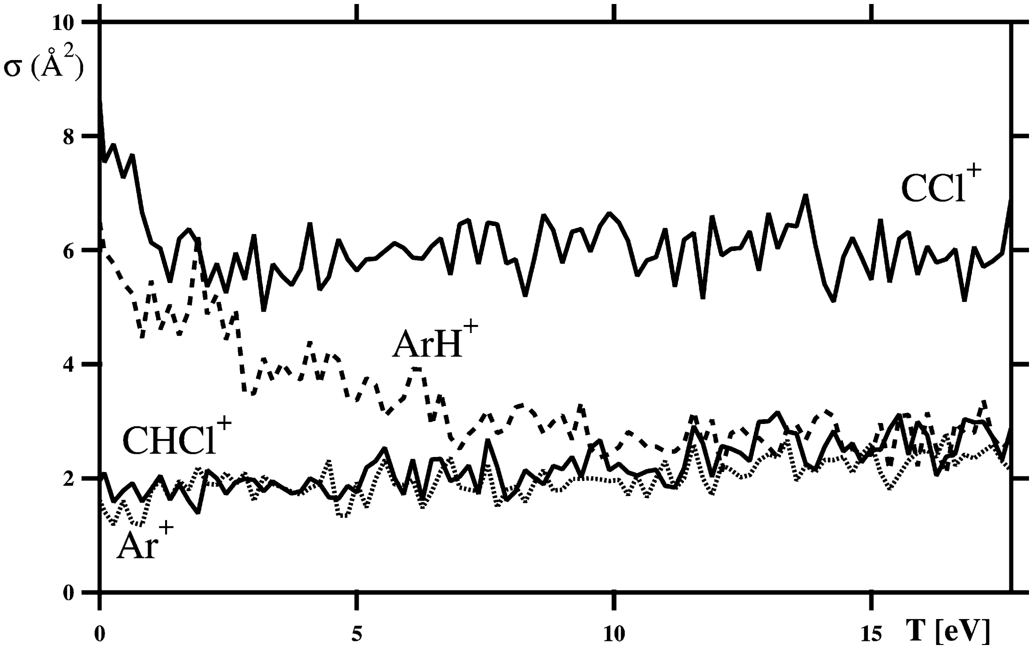

Fig. 2. Absolute integral cross-sections (in Å^2) of ion products in the $CHCl^{2+} + Ar$ system as a function of the c.m. collision energy *T*. As the laboratory energy distribution of the reactant beam (see Section 2) was about 0.5 eV (FWHM), data below about $T = 0.25$ eV should be regarded with caution.

always somewhat lower than those for $CHCl^+$ and CCl^+.

The cross-sections for the charge transfer products, reaction (1), are almost independent of the collision energy. The cross-sections for the products of the proton transfer reaction (2) clearly increase at low collision energies. However, there is a certain difference between this increase: for ArH^+, it starts increasing below 10 eV, while for CCl^+ only below about 2 eV. The difference at higher collision energy may be due to the additional formation of CCl^+ by further dissociation of the charge transfer product (reaction (3)), as indicated by the beam scattering results, and/or by an increased discrimination against back-scattered ArH^+ at higher collision energies.

Small amounts of Cl^+ and CH^+ in the mass spectrum in Fig. 1 are presumably due to the collision-induced dissociation of the reactant dication on Ar

$$CHCl^{2+} + Ar \rightarrow Cl^+ + CH^+ (+Ar) \qquad (4)$$

This explanation is corroborated by an increase of the Cl^+ signal with increasing collision energy (see Fig. 3).

3.2. The $CHCl^{2+} + D_2$ system

In beam scattering studies of this system [13], three reaction products were observed, namely $CHCl^+$, $CHDCl^+$, and CCl^+. The first product, $CHCl^+$, was shown to be formed mainly in the non-dissociative charge transfer reaction of the $CHCl^{2+}$ isomer, $CClH^{2+}$

$$CClH^{2+} + D_2 \rightarrow CClH^+ + D_2{}^+ \qquad (5)$$

$CHDCl^+$ results from the chemical reaction (both isomers of $CHCl^{2+}$ can react, see details in [13])

$$CHCl^{2+} + D_2 \rightarrow CHDCl^+ + D^+ \qquad (6)$$

in two different product ion structures characterized by a different translational energy release. Formation of CD_2Cl^+ was not observed.

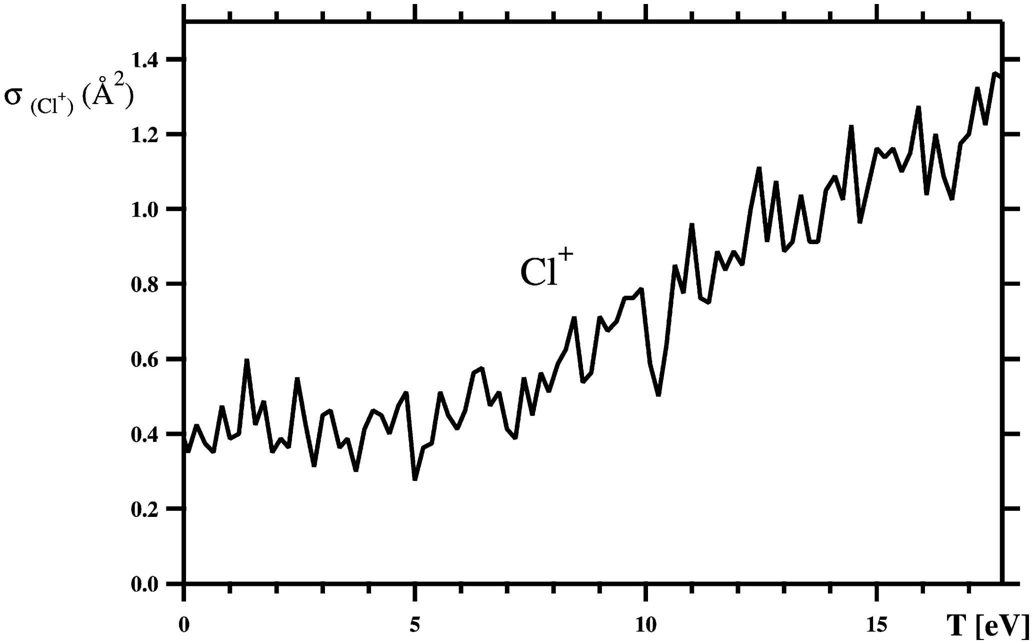

Fig. 3. Absolute integral cross-section (in Å^2) for the formation of the collision-induced dissociation product Cl^+ as a function of the c.m. collision energy *T*.

Finally, analysis of the data suggested that CCl^+ was formed in a proton transfer reaction with a large translational energy release

$$CHCl^{2+} + D_2 \rightarrow CCl^+ + HD_2{}^+ \tag{7}$$

and a small amount of it by further dissociation of the molecular ion product from reaction (6)

$$CHDCI^+ \rightarrow CCl^+ + HD \tag{8}$$

However, direct detection of $HD_2{}^+$ as the other reaction product of reaction (7) in the crossed beam experiments was not fully conclusive.

In the guided beam experiments on reactions in the $CHCl^{2+} + D_2$ system, the mass spectrum of reaction products showed all the three above mentioned reaction products, i.e., $CHCl^+$, $CHDCl^+$, and CCl^+. No CD_2Cl^+ product was formed; this indicates that there is no H–D scrambling in reaction (6). A specific search for the other reaction products unambiguously proved the formation of $D_2{}^+$ and $HD_2{}^+$, as can be seen in the enlarged mass spectrum between *m*/*z* 1 and 9 shown in Fig. 4. However, it should be noted that the registration was difficult and the ion intensities confirm the presence of these ions rather than their true relative intensities. This is why these ions are not shown in the collision energy dependence of the cross-section.

Fig. 5 summarizes the results of measuring the collision energy dependence of the integral cross-sections of formation of the $CHCl^+$, $CHDCl^+$, and CCl^+ product ions of reactions (5)–(7). Because of difficulties in an accurate determination of the deuterium concentration in the reaction region, the data are given in arbitrary units only. However, the data for various reactions are mutually comparable. The integral cross-sections values were of the same order of magnitude as the integral cross-sections of the reactions with Ar. The lines refer to the results of the guided beam experiments. For comparison, the points show the integral cross-sections as derived from the crossed beam scattering studies between 0.5 and 2.5 eV [13], normalized arbitrarily to the value for CCl^+ at 1.5 eV. The agreement between the results is quite good as far as the branching ratio is concerned and also for the values above about 0.7 eV. At the lowest energies, the

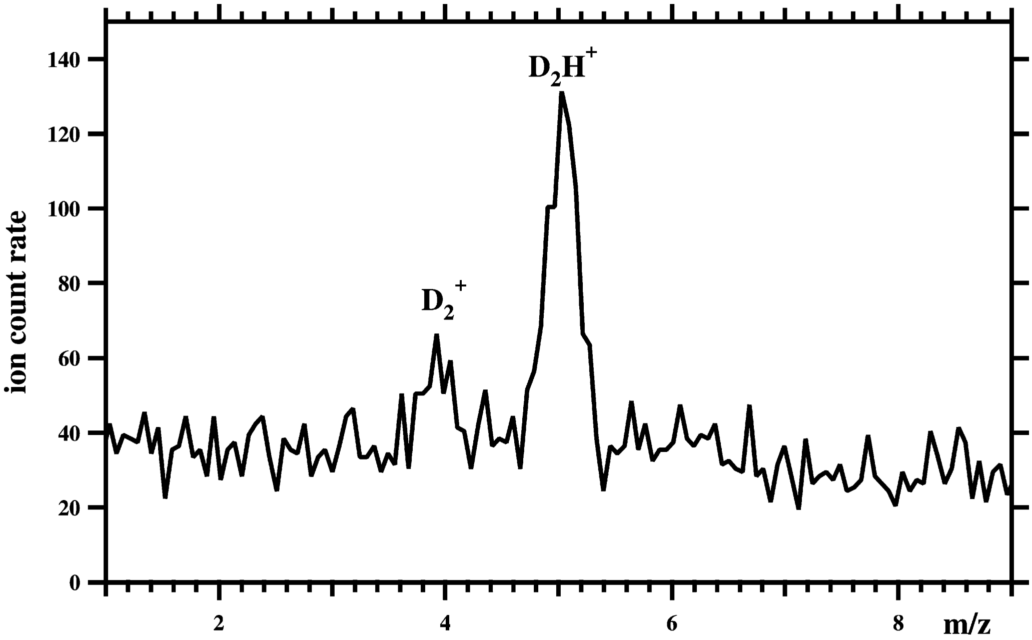

Fig. 4. Mass spectrum of the ion products for the $CHCl^{2+} + D_2$ reaction in the *m/z* range from 1 to 9 (formation of D_2^+ and D_2H^+ reaction products) at the c.m. collision energy of 1.54 eV.

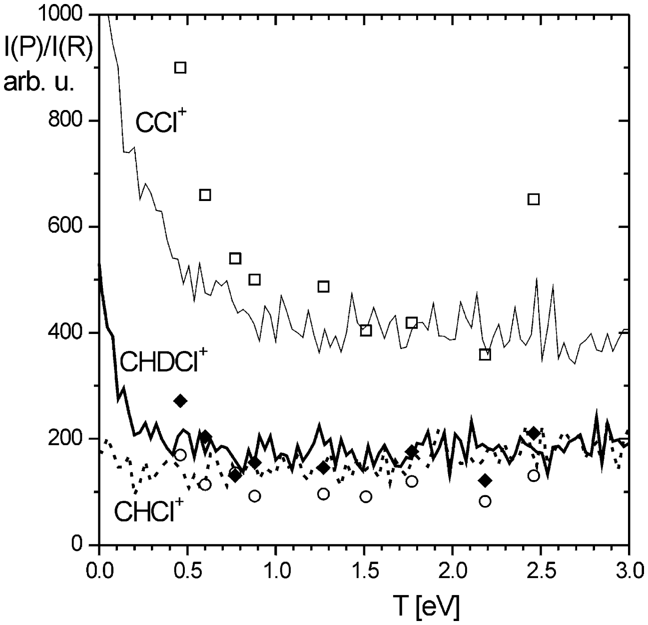

Fig. 5. Integral cross-sections (in arbitrary units) of $CHCl^+$, $CHDCl^+$, and CCl^+ product ions for the reaction between $CHCl^{2+}$ and D_2 as a function of collision energy (c.m.). Points show the results of integral cross-sections derived from the crossed beam scattering experiments [13]: CCl^+ (open squares), $CHCl^+$ (open circles), $CHDCl^+$ (full diamonds). As the laboratory energy distribution of the reactant beam (see Section 2) was about 0.5 eV (FWHM), data below about $T = 0.05$ eV should be regarded with caution.

data derived from the crossed beam scattering tend to increase faster for than those from the present guided beam experiments.

While the cross-section for $CHCl^+$ charge transfer product was practically independent of the collision energy over the collision energy range of 0.1–3.0 eV (center-of-mass, c.m.), the cross-sections for the chemical reactions (6) and (7) showed an increase at collision energies below 0.6 eV.

4. Conclusions

Integral cross-sections of reaction products in the dication-neutral systems, $CHCl^{2+} + Ar$ (absolute values in $Å^2$) and $CHCl^{2+} + D_2$ (values in arbitrary units), were measured in guided beam experiments. The reactant dication was prepared by dissociative double ionization of CH_3Cl by a broad band synchrotron radiation of mean photon energy of about 40 eV. Both singly charged products of ion pairs formed in dication-neutral chemical and charge transfer reactions could be registered, i.e., $CHCl^+ + Ar^+$, $CCl^+ + ArH^+$ in collisions with Ar, and $CHCl^+ + D_2{}^+$, $CHDCl^+$, and $CCl^+ + HD_2{}^+$ in collisions with D_2. The observation of ArH^+ and $HD_2{}^+$ among the reaction products unambiguously confirmed the occurrence of the earlier suggested [13,18] dication-neutral chemical reaction, i.e., proton transfer from the hydrogen-containing molecular dication to the neutral target.

The integral cross-section for the charge transfer processes with Ar was almost independent of the collision energy from about 0.1 to several eV and its value was close to 2 $Å^2$. For the chemical reaction of CCl^+ formation with Ar the integral cross-section was about 6 $Å^2$, with an increase at collision energies below about 1 eV. Integral cross-sections for the reaction with D_2 were of the same order of magnitude.

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