Absolute cross sections for electron impact ionization of Ag$_2$

K. Franzreb, A. Wucher, and H. Oechsner

Fachbereich Physik and SFB 91, Universität Kaiserslautern, W-6750 Kaiserslautern, Federal Republic of Germany

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Abstract. The previously measured relative cross section function for electron impact ionization (EII) of neutral Ag$_2$ has now been calibrated quantitatively by combining the electron impact ionization with in situ non resonant two photon ionization (NR2PI). By comparing the NR2PI saturation intensities measured for Ag$_2^+$ and Ag$^+$ with the corresponding EII intensities, the ratio between the electron impact ionization cross sections (EIICS) of neutral Ag$_2$ and Ag was determined to be $\sigma_{\text{Ag}_2}/\sigma_{\text{Ag}} = 1.53$ for an electron energy of 46 eV. This result agrees well with the geometric $n^{1/3}$ rule ($\sigma_x \sim n^{1/3}$) commonly proposed for the dependence of the EIICS of clusters $X_n$ on the cluster size $n$.

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1. Introduction

In recent years many experimental and theoretical studies have been devoted to the quantitative determination of electron impact ionization cross sections of molecules [1]. Although a large amount of experimental data already exists on this topic, the majority of the experiments have so far been focused mainly to the study of gaseous molecules, hydrocarbons or van der Waals clusters. As a consequence, there are still many target species for which no data are available. A particular example is given by the class of homonuclear metal clusters $X_n$, where due to the complete lack of experimental data the cross sections have to be estimated using theoretical concepts. Two simple empirical formulae have been proposed predicting the dependence of the cross section on the cluster size $n$. First, the additivity rule [2]

$$\sigma_{X_n} = \sigma_X \cdot n$$  \hspace{1cm} (1)

($\sigma_X$: cross section for atom $X$) has been applied to many experimentally determined cross sections and was shown to be a good approximation for a large number of molecules [3, 4]. There are, however, also exceptions where additivity was proven to be not valid [5]. Second, in particular for large homonuclear clusters a modified rule based on geometrical concepts was proposed [6]

$$\sigma_{X_n} = \sigma_X \cdot n^{2/3}.$$  \hspace{1cm} (2)

The present paper is intended to evaluate the validity of either eq. 1 or 2 by an experimental determination of absolute cross sections for neutral silver dimers. For that purpose the electron impact ionization of neutral Ag$_2$ and Ag was combined in situ with saturated photoionization of the same species.

2. Experimental

The experimental setup has been described in detail elsewhere [7]. The neutral atoms and clusters were sputter generated by bombarding a polycrystalline Ag sample under 45° with an Ar$^+$ ion beam of 5 keV. Electron impact ionization of the sputtered neutral silver atoms and dimers as well as mass resolved detection of the ionized species was performed using a commercial quadrupole mass spectrometer equipped with a cross beam electron source. The electron emission current was 0.2 mA. Details of this experiment are given in [7]. In addition, the neutral particles were alternatively ionized by a KrF-eximer laser beam ($\lambda = 248$ nm) perpendicular to both the electron beam axis and the quadrupole axis. The laser was focused into the center of the ionization chamber and, hence, electron impact ionization and photoionization are performed in situ utilising the same neutral beam and ion detection device. The optical setup of the photoionization experiment is described in detail in [8].

Using electron impact ionization, the ratio between the signals measured for Ag$_2^+$ and Ag$^+$ at a specific electron energy $E$ can be described by

$$\frac{I_E(\text{Ag}_2^+)(E)}{I_E(\text{Ag}^+)(E)} = \frac{\sigma_{\text{Ag}_2}(E)}{\sigma_{\text{Ag}}(E)} \cdot \frac{n_{\text{Ag}_2}}{n_{\text{Ag}}} \cdot \frac{T_{\text{Ag}_2}}{T_{\text{Ag}}}.$$  \hspace{1cm} (3)
where \( n_x \) is the number density of neutral particles \( X \) within the ionizing region and \( T_X \) denotes the mass spectrometer transmission and detection probability for \( X^+ \). Hence, for a quantitative evaluation of \( \frac{\sigma_{Ag_2}(E)}{\sigma_{Ag}(E)} \) the other factors entering (3) have to be determined. In principle, this can be achieved from the photoionization experiment provided the laser power density \( P_L \) is high enough to saturate the ionization process, i.e., the measured signal \( I_L(X^+) \) becomes independent of \( P_L \). Then, the ratio between the saturated photoion signals \( I_L^S(X^+) \) is given by

\[
\frac{I_L^S(Ag_2^+)}{I_L^S(Ag^+)} = \frac{n_{Ag_2}}{n_{Ag}} \cdot \frac{T_{Ag_2^+}}{T_{Ag^+}}. \tag{4}
\]

Here, the index "corr" denotes that the measured signals have to be corrected for photon induced fragmentation of \( Ag_2 \).

When electron impact ionization and photoionization are performed at the same geometrical position, the parameters \( n_x \) and \( T_X^* \) in (3) and (4) are identical and the electron impact ionization cross section ratio can be calculated according to

\[
\frac{\sigma_{Ag_2}(E)}{\sigma_{Ag}(E)} = \frac{I_L(Ag_2^+)(E)}{I_L(Ag^+)(E)} \cdot \frac{I_L^S(Ag_2^+)}{I_L^S(Ag_2^+)}. \tag{5}
\]

3. Results

From the measured photoion signals \( I_L(Ag^+) \) and \( I_L(Ag_2^+) \) as a function of the laser power density \( P_L \), it is clearly seen that the non resonant two photon ionization of neutral \( Ag \) atoms is saturated around \( P_L \approx 10^8 \) W/cm\(^2\) [8]. In contrast, the signal recorded for \( Ag_2^+ \) is found to saturate already around \( 10^7 \) W/cm\(^2\). Hence, the two photon ionization of neutral \( Ag_2 \) must be strongly resonance enhanced. This result, which has also been observed in [9], is understandable since the photon energy of 5.0 eV closely matches the energy required for the \( X \rightarrow E \) transition in \( Ag \) [10]. As a consequence, in the limit of low laser power density \( P_L \leq 10^6 \) W/cm\(^2\) the role of photon induced fragmentation can be studied. From the measured photoion signals we find that in this regime the ratio \( I_L(Ag_2^+)/I_L(Ag^+) \) is independent of \( P_L \) [8]. Since two photon ionization of neutral \( Ag \) is obviously negligible in this region, we conclude that the observed \( Ag^+ \) is produced by dissociative ionization of neutral \( Ag_2 \)

\[ Ag_2 + 2hv \rightarrow Ag^+ + Ag + e^- \]

characterized by the cross section \( \beta_{di} \). Hence, the ratio between the cross section \( \beta_L \) for direct photoionization of \( Ag_2 \) and \( \beta_{di} \) is evaluated from \( I_L(Ag_2^+)/I_L(Ag^+) \) as

\[
\frac{\beta_L}{\beta_{di}} = 2.1 \pm 0.2. \tag{6}
\]

This agrees well with the corresponding results of [9]. From (6) the saturated photoion signals can now be corrected for dissociative photoionization of \( Ag_2 \) by

\[
I_L^S(Ag_2^+) = I_L^S(Ag_2^+) \cdot [1 + \beta_{di}/\beta_L]
\]

\[
I_L^S(Ag^+) = I_L^S(Ag^+) - \beta_{di}/\beta_L \cdot I_L^S(Ag_2^+). \tag{7}
\]

The situation is more complicated, however, if neutral photodissociation of \( Ag_2 \) is to be taken into account. Here, a straightforward correction cannot be applied. In order to get a feeling for the magnitude of this influence, we positioned the laser beam into the free space between the target and ionization chamber (see Fig. 1). Now, the laser was only employed for neutral fragmentation of \( Ag_2 \) while the electron beam was used to probe the remaining flux of neutral \( Ag_2 \). The signal detected for \( Ag_2^+ \) in this manner did not change observably when the laser was switched on or off. Hence, the role of neutral photodissociation of \( Ag_2 \) seems to be small in the present case.

From the intensities measured for electron impact ionization of \( Ag_2 \) and \( Ag \) with an arbitrarily chosen electron energy of \( E = 46 \) eV and the saturated photoion signals we obtain

\[
\frac{I_E(Ag_2^+)}{I_E(Ag^+)} = 0.31 \quad \text{and} \quad \frac{I_L^S(Ag_2^+)}{I_L^S(Ag_2^+)} = 4.96
\]

and, hence,

\[
\frac{\sigma_{Ag_2}}{\sigma_{Ag}} = 1.53 \pm 10\%
\]

for an electron energy of \( E = 46 \) eV. Accordingly, Fig. 1 shows the measured cross section ratio \( \sigma_{Ag_2}/\sigma_{Ag}(E) \) calibrated at \( E = 46 \) eV. As seen from the figure, this ratio is nearly independent of the electron energy for \( 50 \) eV \( \leq E \leq 120 \) eV. In connection with the absolute value of 1.53, this finding is in good agreement with the geometric \( n^{1/3} \)-rule (yielding 1.59 for dimers), although this rule was originally derived for large clusters consisting of many atoms and should, strictly speaking, not apply to dimers. Our data can, however, also be interpreted in terms of the additivity rule (1) if it is kept in mind that (1) is expected to describe total rather than partial ionization cross sections. Hence, in this interpretation the difference between the expected cross section ratio of 2 and the measured value of 1.53 would be attributed to dissociative

![Fig. 1. Ratio of electron impact ionization cross sections of neutral \( Ag_2 \) and \( Ag \) vs. electron energy](attachment:image.png)
Fig. 2. Absolute cross section for electron impact ionization of neutral Ag₂ and Ag vs. electron energy.

Ionization of Ag₂ by electron impact and the respective cross section would be $\sigma_{\text{Ag}_2}^{\text{II}} = 0.31 \sigma_{\text{Ag}_2}$ for an electron energy of 46 eV.

Using data on the absolute cross section of Ag atoms published by Freund et al. [11], we determine an absolute cross section of $\sigma = 8.34 \cdot 10^{-16}$ cm² for electron impact ionization of Ag₂ at $E = 46$ eV. Figure 2 shows the resulting behaviour of the cross section $\sigma_{\text{Ag}_2}$ as a function of the electron energy $E$. For completeness the measured atomic cross section (which was also calibrated at $E = 46$ eV from [11]) has been included in the figure. Details of the calibration of $E$ are given in [7]. Due to the error bar of approx. 10% stated in [11], the error of the absolute calibration of $\sigma_{\text{Ag}_2}$ is estimated to be $\leq 20\%$.

References