INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **34** (2001) 1415–1423 www.iop.org/Journals/jb PII: S0953-4075(01)20310-1

Dissociative electron attachment to hydrogen

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Received 22 December 2000, in final form 13 February 2001

Abstract

Using two different crossed-beams high-resolution electron attachment instruments (employing either a trochoidal electron monochromator or a hemispherical electron monochromator) we have determined the cross section curve for H^- production from H_2 via the 4 eV resonance at two different temperatures. These relative partial cross sections have been calibrated by comparing present values for the 14 eV resonance with absolute total cross sections determined previously. Taking into account the experimental energy distribution and the rotational excitation and its influence on the cross section shape we obtain very good agreement with theoretical predictions in terms of both the shape and magnitude of this resonance peak.

1. Introduction

The discovery of large concentrations of H^- ions ($\geqslant$30%) in low-temperature hydrogen plasmas [1] has provided the possibility of producing intense beams of H^- ion sources for neutral beam heating [2,3] of thermonuclear fusion devices [4,5]. Modelling of such plasmas requires a detailed knowledge of the mechanism of dissociative electron attachment (DEA) of electrons to molecular hydrogen. Schematically the process may be written as a two-step process:

$$e^- + H_2(v, J) \rightarrow H_2^- \rightarrow H^- + H \tag{1}$$

where v and J denote the vibrational and rotational quantum numbers of the target hydrogen molecule. The incident electron is trapped by the neutral molecule in a resonant state, this trapping increasing the electron residence time sufficiently to allow the relatively slow moving nuclei to dissociate. In the present case the $H_2^-(1\sigma_g^2 1\sigma_u\ ^2\Sigma_u^+)$ resonance formed at

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0953-4075/01/081415+09$30.00

a range of electron energies of around 4 eV is characterized by a very short lifetime against autodetachment when formed from the $v = 0$ level. Hence the cross section for product H^- is low. However, previous measurements [6, 7] have shown that the cross section for DEA increases dramatically with the internal energy of the target, since the survival probability associated with the excited nuclear-motion anion states increases rapidly as the internuclear separation of the neutral target becomes larger. For example, the cross section rises by four orders of magnitude when the vibrational level in H_2 is raised from $v = 0$ to 4 [6]. This rapid change in cross section has been used by Hall and co-workers to probe the internal energy of molecular hydrogen formed by atomic recombination on many surfaces [8–11] and to probe the internal energy of hydrogen molecules in gaseous discharges [12].

The effect of rotation on the cross section is also dramatic (a five-fold increase from $J = 0$ to 7 [6]) and rather significant for plasma oriented work since with increasing J the threshold for H^- production is lowered with each increase in J. This has important consequences in low-temperature plasmas since the energy distribution of the electrons may change rapidly over small regions and thus nascent H^- production may increase dramatically as higher rotational states are excited in the plasma.

Several theoretical groups [13–20] have calculated the behaviour of the cross section for H^- production from H_2 ($v = 0$) close to the $v = 0$ threshold and, whilst the general shape is agreed (an extremely rapid onset followed by a slow fall), the exact profile remains uncertain, in particular the width of the resonance varies from between 340 meV [14, 16] and 500–530 meV [13, 15, 17, 18]. Previous experiments [19] partly limited by the resolution of the incident electron beam have not shown this extremely rapid onset of the leading edge (also see the inset in figure 1 of [6]) and cannot be used to resolve the discrepancies in magnitude between the theories (figure 1). Therefore, using two different independent high-resolution electron attachment apparatus, we have remeasured the cross section for H^- production from H_2 via the 4 eV resonance. The role of rotational excitation of the target is taken into account using recently calculated data by Fabrikant [20] and measured cross sections compared with available theoretical calculations.

2. Experiment

The present experiments were performed using two different crossed electron/molecule beam apparatus which have been described in detail before [21, 22]. In the first apparatus [21] a high-resolution trochoidal electron monochromator is used to produce electron beams with an optimum resolution of about 5 meV (FWHM) close to zero energy and of about 50 meV at higher energies [23, 24]. In the second apparatus [22] a hemispherical monochromator was used to produce electron beams with an optimum resolution of about 30 meV [25]. Due to the low cross section ($\sim 10^{-21}$ cm^2, see below) for H^- production it was necessary to operate both instruments at lower resolutions (100–200 meV) to maximize the available electron current and thus the ion signals. In both cases the attachment reactions occur in a small collision chamber from which the anions are extracted by a weak homogeneous electric field into a quadrupole mass spectrometer. The mass selected H^- ions were detected in a single-ion pulse counting mode using a channel electron multiplier. Both apparatus used a PC to control data acquisition during the measurements. The electron energy scale and electron beam resolution were calibrated and determined throughout the experiment by monitoring the Cl^- yield from CCl_4 [24] or recently also by retarding field analysing systems [23].

The molecular hydrogen target gas was produced by a simple capillary operated under conditions of effusive flow in the case of the TEM instrument and as a stagnant gas in the case of the HEM instrument. The ro-vibrational temperature of the hydrogen beam was therefore

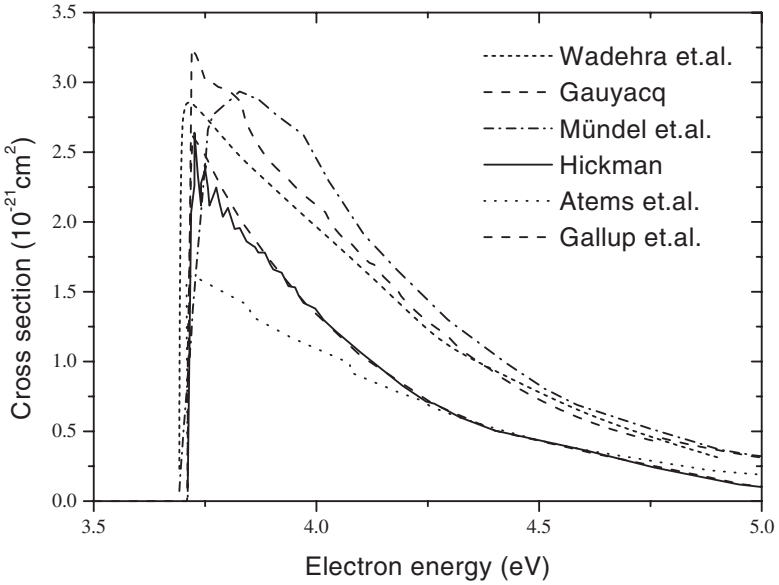

Figure 1. Calculated cross section functions for DEA to $H_2(v = 0, J = 0)$ reported by [13–18].

assumed to be in thermal equilibrium with the apparatus (400 K for the trochoidal instrument due to constant heating of the apparatus and 300 K for the hemispherical instrument operated at room temperature). It is then possible to derive the rotational state population distribution using a simple Boltzmann statistical model taking also into account the even–odd alternations specified by nuclear spin statistics (1 : 3 in H_2 for parahydrogen to orthohydrogen) favouring strongly the presence of the odd rotational states. Since the vibrational spacing in H_2 is large ($v(1) - v(0) = 516$ meV) it may be assumed that no vibrationally excited molecules are present in the target beam used.

3. Results and discussion

The H^- yields measured (after subtracting background contributions to the H^- yield) in the two apparatus are shown in figure 2. The results obtained in the two different instruments (i.e., the shape of the relative partial cross section functions) are in agreement if we allow for the better resolution in the hemispherical instrument as compared to the trochoidal instrument used in these two experimental runs (100 versus 200 meV, respectively). Moreover, allowing for the different resolutions used the present relative partial cross section data are also in agreement with the previous experiment of Schulz and Asundi [19] (see open circles in figure 2) using the retarding potential difference method with a FWHM of about 100 meV. The line shape obtained by [19] has been confirmed in a follow up experiment on the vibrational and rotational excitation in dissociative attachment to H_2 by Allan and Wong [6] using a trochoidal monochromator.

The observed cross sections are a combination of the apparatus function of the instrument (as given by the FWHM of electron energy distribution) convoluted with the DEA cross sections from summed J states of $H_2(v = 0)$. Therefore in order to compare experiment directly with theory it is necessary to weigh the cross section of each rotational state of the $H_2(v = 0)$ target molecules with its population probability at the specific gas temperature and then convolute this sum with a (Gaussian) apparatus function accounting for the electron energy distribution. It is

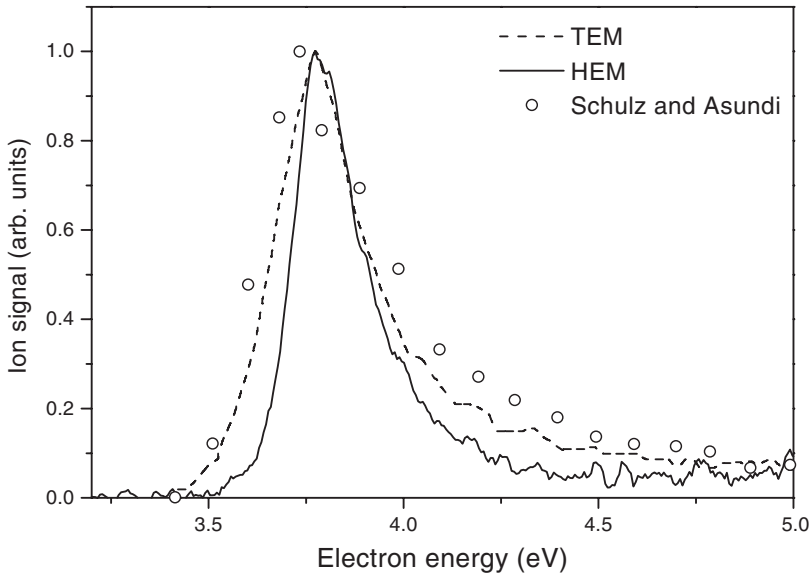

Figure 2. Comparison between relative H^- yields measured in the trochoidal (designated TEM) instrument with a 200 meV resolution and at a gas temperature of 400 K and in the hemispherical (designated HEM) instrument with a 100 meV resolution at a gas temperature of 300 K. For comparison we also show (designated by open circles) the results of the previous experiment of Schulz and Asundi [19] using the retarding potential difference method with a FWHM of about 100 meV. All three curves have been normalized in height to each other at the maximum cross section value.

interesting to note that in some of the earlier papers theoretical curves for H_2 ($v = 0$) have been compared with the data of Schulz and Asundi [19] without taking into account a broadening of the leading edge by the population of rotational states, thus arriving at the wrong conclusion that there exists even after taking into account the electron energy distribution a discrepancy between experiment and theory. Assuming that the weighing of the rotational distributions may be derived from a simple Boltzmann distribution at the corresponding temperature (300 and 400 K, respectively, in the present experiments) allowing also for the nuclear-spin statistics and that the ratios of the rotational cross sections are those predicted by Fabrikant [20], for each of the theoretical calculations for $v = 0$ shown in figure 1 the resulting summed cross sections were convoluted with the electron energy distribution and compared with experimental results.

A detailed comparison shows that the present cross sections are, in terms of magnitude (see below) and shape, more consistent with the calculations of Hickman [16] (shown in figures 3 and 4 together with our data) and Gauyacq [14] predicting a narrower resonance than those of Wadehra and co-workers [13, 17], Mündel *et al* [15] or Gallup *et al* [18]. Moreover, the agreement in the onset and the shape of the leading edge is especially noteworthy (see the upper panel of figure 4 where the two cross section curves have been normalized in height to each other at the maximum thus allowing a comparison of the shape independent of the additional uncertainty in absolute cross section values, see below). It is interesting to note that the resonance theory of Wadehra and co-workers [13, 17] and the effective-range theory of Gauyacq [14], although different in physics, are both semi-empirical. In contrast, the treatments of Mündel *et al* [15] and Gallup *et al* [18] are completely *ab initio*. Hickman [16] basically uses the model of Mündel *et al* [15], but makes the open-channel approximation in the treatment of the complex potential and uses non-parametrized potential curves. The fact that

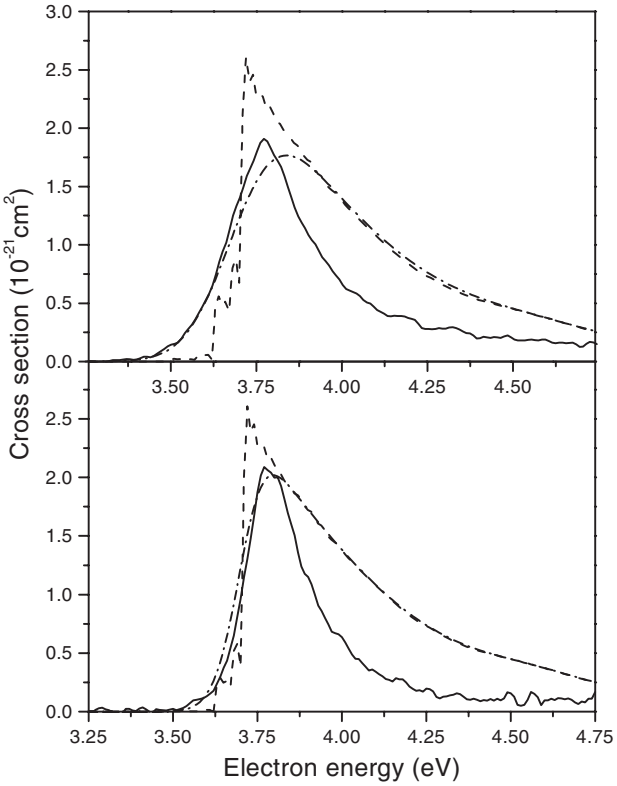

Figure 3. The theoretical data of Hickman [16] weighted with the population probability for each rotational state using the data of Fabrikant [20] (designated by the dashed curve) and convoluted with the apparatus function (designated by the dot-dashed curve) compared to the present TEM experimental data obtained with a resolution of 200 meV (full curve in the upper panel) and to the present HEM experimental data obtained with a resolution of 100 meV (full curve in the lower panel). The experimental data have been calibrated absolutely using the technique described in the text.

the present experimental data agree so well with those of Hickman apparently indicates that very accurate (non-parametrized) potential curves should be used, especially in the crossing region. This good agreement also indicates that the absolute energy calibration carried out in both instruments leads to a very accurate (linear) energy scale. The agreement is best in the case of the TEM instrument (where the electron energy distribution can be described very well by a Gaussian function). However, all of the present theories (except the *ab initio* calculation of Robineaux [26] which appears to closely follow the experimental data of Schulz and Asundi [19] in the energy range 3.75–5.0 eV given, see figure 7 in [26]) seem to overestimate the width of the resonance when compared to experiment.

One possible explanation for this discrepancy in the width of the resonance between theory and experiment is the apparatus discrimination against H^- ions with higher kinetic energies. The energetics of the dissociative attachment process may be written as

$$E_e + E_{v,J} = E_f + D_0 - \mathrm{EA} \tag{2}$$

where E_e is the incident electron energy, $E_{v,J}$ the internal ro-vibrational energy of the neutral target, E_f the translational energy of the fragments, D_0 the dissociation energy with respect to the lowest ro-vibrational state (4.447 eV) and EA the electron affinity (0.754 eV). At threshold

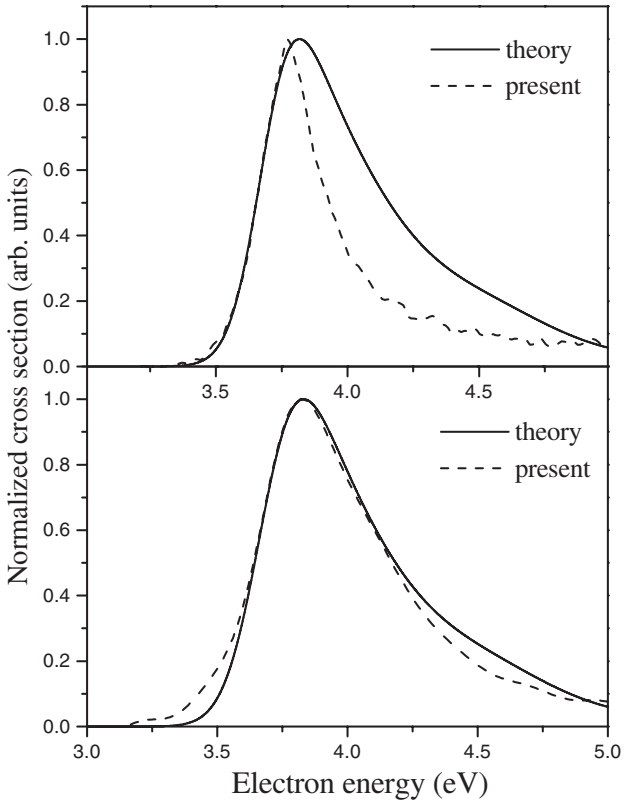

Figure 4. The theoretical data of Hickman [16] weighted with the population probability for each rotational state using the data of Fabrikant [20] and this sum convoluted with the apparatus function compared to the present TEM experimental data obtained with a weak extraction field (upper panel) and with a larger extraction field (lower panel). The experimental and theoretical curves have been normalized in height with each other at its maximum value. The experimental data in the lower panel had to be shifted by 98 meV to higher energy in order to achieve agreement between the two curves.

the fragment energy, E_f, is zero and therefore only a small extraction field is needed to focus the product H^- ions into the quadrupole mass spectrometer but, as the incident energy increases, so does the kinetic energy of the H^- ions and thus larger extraction fields are required to focus the ions into the quadrupole. Therefore if a fixed extraction voltage is used it is possible that as the incident energy increases the proportion of H^- ions detected falls hence artificially producing a lower cross section at higher energies (see a detailed study on this phenomenon in the case of O^- production from CO in [22] and references given therein). However, a higher extraction voltage produces a poorer energy resolution since the extraction voltage penetrates into the collision chamber (see [22]). It is therefore necessary to select an extraction voltage high enough to collect the majority of the H^- ions at all incident electron energies but to simultaneously allow electron beams of sufficient resolution to be used to probe the rapid onset at threshold.

In the present experiment a range of extraction voltages were used to probe the ion collection efficiency of the TEM apparatus, two of which are shown in figure 4. Using a weak extraction field the measured yields are in good agreement with the previous experiment of Schulz and Asundi [19] (see the comparison shown in figure 2) suggesting that the previous

data discriminated against H^- ions with large kinetic energies. Using larger extraction fields the yield of H^- ions at higher incident electron energies is increased and is in closer agreement with the calculation of Hickman [16] (using the rotational data of Fabrikant [20]) although the theory still appears to overestimate the cross section at higher energies.

The absolute cross section for DEA via the 4 eV resonance, and hence the rate constants, are of utmost importance in gas discharge and fusion plasma modelling [2–5]. The values most commonly used for comparison with theory and most commonly quoted in the literature are those derived by Schulz and Asundi in 1967 [19] using for the normalization of their measured H^- yield the total cross section measurement by Schulz [27], i.e. yielding for the maximum of the 4 eV resonance a value of 1.6×10^{-21} cm^2. As the values given by [19] are not deconvoluted for the energy resolution of their apparatus they will necessarily lie below the theoretical values. Schulz and Asundi obtained absolute DEA cross sections at the 4 eV resonance by comparing their measured negative ion currents at the maximum of the 4 eV resonance with those at the maximum of the 14 eV resonance (arguing that in both cases ions are formed with equally low kinetic energy thus having equal detection efficiencies) and using for the 14 eV process absolute cross sections from the literature. For the 14 eV peak two absolute values are reported in the literature, both experiments using a total-ionization tube to determine the cross sections, namely 2.08×10^{-20} cm^2 by Schulz [27] and 3.5×10^{-20} cm^2 by Rapp *et al* [28]. This large discrepancy was noted and discussed by Rapp *et al* [28] and arguments are given in favour of their much larger value. Nevertheless, in their normalization procedure Schulz and Asundi [19] used the much smaller value of Schulz [27]. In contrast, here we use (see the results shown in figure 3) the absolute value of Rapp *et al* [28] thus taking into consideration the great success and accuracy of their positive cross sections (still used today as benchmark data in the field of electron impact ionization [29]) measured with the same apparatus.

Since both H^- ions produced at the leading edge of the 14 and the 4 eV peaks have essentially zero kinetic energy, the cross section ratio measured should be free of any ion kinetic energy discrimination. The ratio of the H^- yield at the thresholds should therefore be the same in all the experiments. In the present experiment the yield of H^- ions at the 4 eV resonance is about 10% in the case of the HEM instrument and about 9% in the case of the TEM instrument of those produced at 14 eV, while Schulz and Asundi [19] report about 8%. As the convolution of the sharp 4 eV peak with the experimental energy spread will lower the cross section by different amounts, the differences in this ratio can be easily understood in terms of the different energy resolutions used, i.e. 100 meV for the HEM, 200 meV for the TEM and approximately 450 meV by Schulz and Asundi [19] (they mention that their absolute cross sections have been derived without using the RPD method). Figure 3 shows the presently obtained absolute cross sections in comparison with the calculated values of Hickman [16] using the rotational data from Fabrikant [20]. It can be seen that in both cases very good agreement exists between the experimental data (using the absolute cross section of Rapp *et al* [28] for calibration) and the theoretical data (taking into account the differing energy resolutions). On the one hand this proves that the different ratios obtained (10 and 9%) are indeed due to the different energy resolutions and that the use of the absolute data set from Rapp *et al* for calibration gives very satisfactory agreement with absolute theoretical cross sections. Therefore, at present we recommend to use instead of the usually reported value from Schulz and Asundi [19] of 1.6×10^{-21} cm^2 the present data sets (either the experimental ones for practical purposes, giving at about 4 eV a value of about $2.2–1.8 \times 10^{-21}$ cm^2, respectively, depending on the energy resolution, or the theoretical calculation from Hickman for modelling, having a maximum value of about 2.7×10^{-21} cm^2). It is interesting to note that Cizek *et al* [30] have recently extended their *ab initio* nonlocal resonance theory [15] to

treat DEA of rotationally excited H_2 molecules and calculated the cross section for hot H_2 molecules ($T = 1400$ T). This allows comparison with the data of Allan and Wong [6] after normalization of these data. Using for this normalization the data of Schulz and Asundi [19] it turns out that the maximum value of the experimental data of Allan and Wong [6] is three times less than the theoretical prediction (see figure 6 in [30]). Using, however, the present results for calibration would immediately improve the agreement for this case.

4. Conclusions

The present experimental studies suggest that previous experimental cross sections reported by Schulz and Asundi [19] for dissociative attachment to H_2 underestimate the cross sections at the high-energy side of the 4 eV peak due to energy discrimination of the product ions. The present data are, in magnitude and shape, in better agreement with the calculations of Hickman [16] and Gauyacq [14] than the more commonly quoted data of Atems and Wadehra [17] and we therefore suggest that the values of [14] and [16] should be used in the modelling of hydrogen plasmas.

Improvements being made in the present apparatus will shortly allow us to measure the absolute profile of the DA cross section for H^- from H_2 yet more accurately, using larger ion extraction fields and better electron energy resolutions. A new normalization technique [31] will also allow new absolute values for the DA cross section to be reported. Detailed investigations of both the isotopic [32] and temperature dependence will also be studied such that, after 30 years, definitive experimental cross sections for this important collision process will finally be established.

Acknowledgments

This work has been partially carried out within the Association EURATOM-ÖAW and also supported by the FWF, Wien, Austria and the Royal Society, United Kingdom. It is a pleasure to thank Professor I Fabrikant, Lincoln, for helpful discussions and for providing his data for rotational excited states [20] prior to publication.

References

[1] Nicolopoulou E, Bacal M and Doucet H J 1977 *J. Physique* **38** 1399
[2] Graham W G 1995 *Plasma Sources Sci. Technol.* **4** 281
[3] Cacciatore M A, Capitelli M and Celiberto R 1992 *At. Plasma Mater. Interaction Data Fusion* **2** 65
[4] Janev R K 1995 *Atomic and Molecular Processes in Fusion Edge Plasmas* (New York: Plenum)
[5] Mohr P and Wiese W L 1998 *Atomic and Molecular Data and their Applications (AIP Conf. Proc. vol 434)* (Woodbury: AIP)
[6] Allan M and Wong S F 1978 *Phys. Rev. Lett.* **41** 1791
[7] Popovic S, Cadez I, Landau M, Pichou F, Schermann C and Hall R I 1990 *Meas. Sci. Technol.* **1** 1041
[8] Cadez I, Hall R I, Landau M, Pichou F and Schermann C 1997 *J. Chem. Phys.* **106** 4745
[9] Gough S, Schermann C, Pichou F, Landau M, Cadez I and Hall R I 1996 *Astron. Astrophys.* **305** 687
[10] Schermann C, Pichou F, Landau M, Cadez I and Hall R I 1994 *J. Chem. Phys.* **101** 8152
[11] Cadez I, Schermann C, Landau M, Pichou F, Popovic D and Hall R I 1993 *Z. Phys.* D **26** 328
[12] Schermann C, Hall R I, Landau M, Pichou F and Cadez I 1990 *AIP Conf. Proc.* vol 210 p 159
[13] Wadehra J M and Bardsley J N 1978 *Phys. Rev. Lett.* **41** 1795
[14] Gauyacq J P 1985 *J. Phys. B: At. Mol. Phys.* **18** 1858
[15] Mündel C, Berman M and Domcke W 1985 *Phys. Rev.* A **32** 181
[16] Hickman A P 1991 *Phys. Rev.* A **43** 3495
[17] Atems D E and Wadehra J M 1990 *Phys. Rev.* A **42** 5201

[18] Gallup G A, Xu Y and Fabrikant I I 1998 *Phys. Rev.* A **57** 2596
[19] Schulz G J and Asundi R K 1967 *Phys. Rev.* **158** 2
Schulz G J and Asundi R K 1965 *Phys. Rev. Lett.* **15** 946
[20] Fabrikant I I 1999 Private communication
Xu Y, Gallup G A and Fabrikant I I 2000 *Phys. Rev.* A **61** 052705
Xu Y, Kazansky A K and Fabrikant I I 2000 *Phys. Rev.* A **63** 014703
[21] Matejcik S, Kiendler A, Stampfli P, Stamatovic A and Märk T D 1996 *Phys. Rev. Lett.* **77** 3771
[22] Denifl G, Muigg D, Stamatovic A and Märk T D 1998 *Chem. Phys. Lett.* **288** 105
[23] Grill V, Drexel H, Sailer W, Lezius M and Märk T D 2001 *Int. J. Mass Spectrom.* **205** 209
[24] Matejcik S, Senn G, Scheier P, Kiendler A, Stamatovic A and Märk T D 1997 *J. Chem. Phys.* **107** 8955
[25] Denifl G, Muigg D, Walker I, Cicman P, Matejcik S, Skalny J D, Stamatovic A and Märk T D 1999 *Czech. J. Phys.* **49** 383
[26] Robineaux F 1991 *Phys. Rev.* A **43** 5946
[27] Schulz G J 1959 *Phys. Rev.* **113** 816
[28] Rapp D, Sharp T E and Briglia D D 1965 *Phys. Rev. Lett.* **14** 533
[29] Märk T D and Dunn G H 1985 *Electron Impact Ionization* (Vienna: Springer)
[30] Cizek M, Horacek J and Domcke W 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 2671
[31] Matt S, Dünser B, Lezius M, Deutsch H, Becker K, Stamatovic A, Scheier P and Märk T D 1996 *J. Chem. Phys.* **105** 1880
[32] Cadez I, Hall R I, Landau M, Pichou F and Schermann C 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 3271