

## ELECTRON ATTACHMENT TO MOLECULES AND ITS USE FOR MOLECULAR SPECTROSCOPY

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### Abstract

A short review of the use of electron attachment to molecules for molecular spectroscopy is presented. The main emphasis is given to the vibrational spectroscopy of molecular hydrogen that is based on detection of low-energy H<sup>-</sup> ions from dissociative electron attachment. Some examples of the use of this method are presented.

**Key words:** dissociative electron attachment, vibrationally excited hydrogen molecules, molecular spectroscopy

### Introduction

Electron attachment (EA) to molecules has been studied in much detail since the early sixties.<sup>1</sup> Since that time, negative ions have been used more and more extensively for a variety of spectroscopic applications,<sup>2</sup> and the negative ion option is nowadays a common feature of commercial mass spectrometers.

The main EA process of interest for the present consideration is dissociative electron attachment (DEA):



where, AB is a diatomic or polyatomic target molecule and A and B are fragments that can be either single atoms or molecular radicals. DEA is energetically possible if fragment B has a positive electron affinity, i.e. can form a stable negative ion. As the total energy of the reaction is positive (incident electron energy), the transient negative ion AB<sup>-\*</sup> is unstable. It can be stabilised by autodetaching the extra electron (elastic or

inelastic resonant electron scattering) or by dissociating thus transferring its excess energy to the dissociation process.

The stabilisation of the transient negative ion  $AB^{-*}$  is also possible by a third body collision or photon emission. In this case, a stable parent ion is formed and the process is non-dissociative EA. This process can only happen in a dense gas or in the case where the lifetime of the transient ion is sufficiently long. Typical lifetimes of transient negative ions formed at a few eV electron energy is from  $10^{-16}$  s (e.g.  $H_2$ ) to about  $10^{-11}$  s ( $O_2$ ) so that radiative transitions are of minor importance. However, for EA to polyatomic molecules at very low energies, the lifetime can be as long as  $10^{-2}$  s so that non-dissociative EA can become important.

DEA is a resonant process i.e. it occurs only at the incident electron energies where the corresponding state of the  $(AB^-)$  complex exists. The attached electron transfers all its energy, angular and linear momentum to the target. Therefore, the kinematics of the process is simple and the resulting energy and angular distributions of the fragment ions provide additional possibilities for spectroscopic methods. The energy and angular distributions were studied for many diatomic (e.g.  $CO$ ,<sup>3</sup>  $H_2$ <sup>4</sup>) and polyatomic (e.g.  $CO_2$ <sup>5</sup>) molecules.

Besides the simple kinematics, there is another aspect of DEA that is important for its applicability to spectroscopic methods. This is the dependence of the cross section (CS) on the internal excitation of the target molecule. This effect was first recognised by the temperature dependence of CS but was later treated on the basis of state selective analysis. In the past years, a large amount of evidence on this important effect has been collected.<sup>6</sup> Especially, the spectacular dependence of DEA on initial vibrational excitation was observed for the hydrogen molecule.<sup>7</sup>

The spectroscopic use of EA can be for studies of basic molecular properties (spectroscopy and characteristics of stable and unstable electronic states of negative ions), and as a tool for studying molecular reactions and interactions or as a tool for a particular application.

Some examples of modern spectroscopic use of EA to molecules are the studies of extremely low energy EA,<sup>8,9</sup> EA to clusters<sup>10</sup> and EA to molecules adsorbed on a surface in the form of mono- or multi-layers.<sup>11</sup> Very large cross sections for near-zero energy

DEA to many important contaminants has led to the development of specific instruments capable of trace gas detection.<sup>12,13</sup>

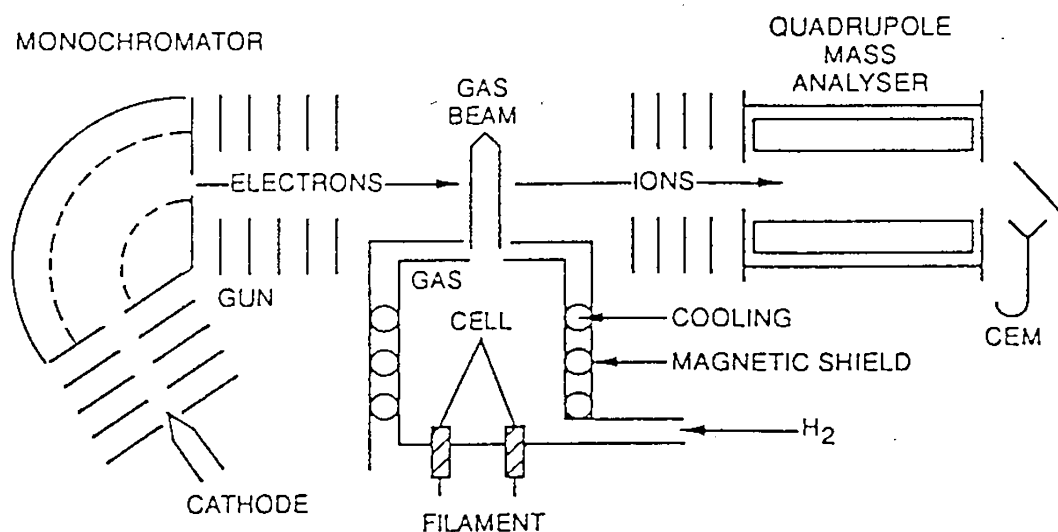
The method for the determination of ro-vibrational populations in hydrogen<sup>14</sup> is described here in some detail as an example of the application of DEA for molecular spectroscopy. This method is based on the strong increase of the DEA cross section in H<sub>2</sub> with ro-vibrational excitation,<sup>7</sup> and the high yield of near-zero energy H<sup>+</sup> ions and has been used for studies of vibrational excitation of hydrogen molecules produced by recombination of hydrogen atoms on surfaces.<sup>15,16,17</sup>

### Experimental method

The experimental method and apparatus are described in detail elsewhere.<sup>14</sup> The method is based on the fact that, for the lowest energy DEA process in hydrogen, "zero" energy ions are produced with high probability at the threshold.<sup>18,19</sup> For the ground vibrational state ( $v=0$ ) this threshold is, according to energy conservation, at  $E_{\text{th}} = D(\text{H}_2) - EA_{\text{H}} = 4.478 - 0.754 = 3.724$  eV ( $D(\text{H}_2)$  - dissociation energy of H<sub>2</sub>;  $EA_{\text{H}}$  - electron affinity of H). If the target molecule is in an excited vibrational state, less energy is needed for dissociation and therefore the DEA threshold for this state will be at a lower incident energy. This, together with the fact that the CS for DEA strongly increases with target excitation, is the basis of the present method. It should be noted that other DEA channels exist at higher incident electron energy leading to more energetic fragments. Higher fragment energy manifests itself as either higher kinetic energy or electronic excitation of the resulting H atom. The same characteristics of DEA are present for all hydrogen isotopomers so this method is also applicable to the HD and D<sub>2</sub> molecule.

The experimental set-up is shown in Figure 1. It basically consists of a low energy electron gun and a zero-energy ion detection system for measurement of the H<sup>+</sup> yield. The low energy electron gun has a thermionic electron source and an electrostatic energy filter with entrance and exit electrostatic lenses. The electron beam crosses at right angles the effusive target gas beam. The low energy ion detection system is placed at right angles to both, the electron and gas beams. This system consists of an extraction optics, acting on the principle of penetrating field, a quadrupole mass spectrometer that transmits only ions of interest and an off-axis channel electron multiplier as ion detector.

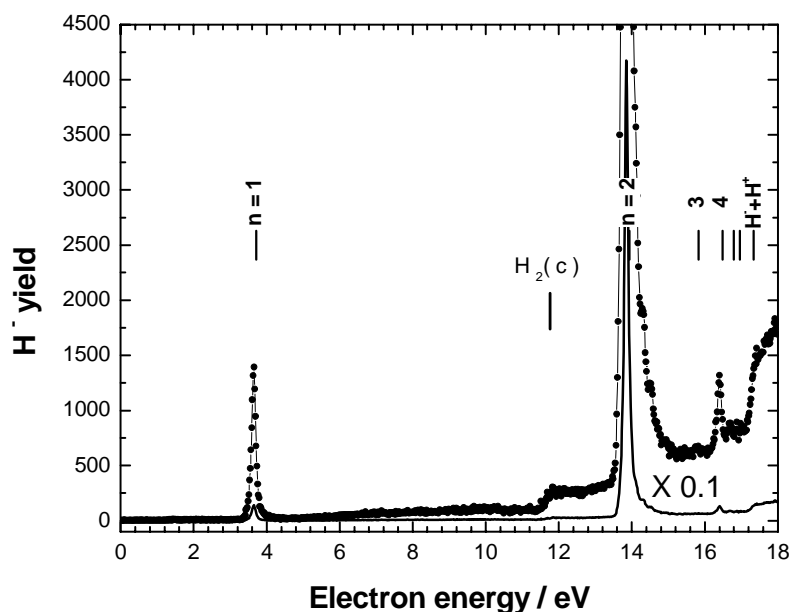
The spectrometer operates so that the energy of the electron beam is scanned between 0 and 5 eV while the ion detection system is tuned for the optimum detection of "zero"-energy ions and is kept constant during data acquisition. In this way, the experimental result is the spectrum of "zero" energy ion yield versus incident electron energy.



**Figure 1.** Schematics of the experimental set-up for determination of the vibrational population distribution in hydrogen.<sup>14</sup>

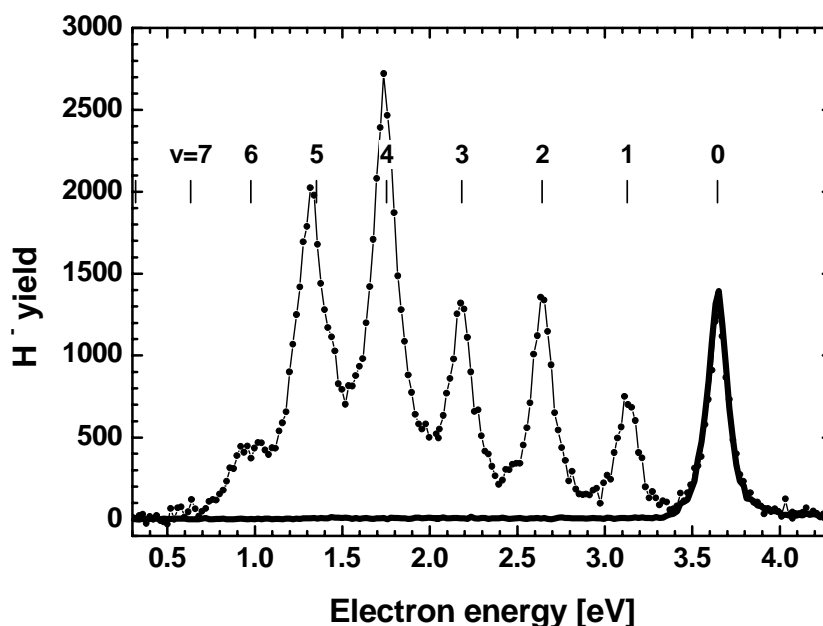
The energy dependence of H<sup>-</sup> yield in the wide range from 0 to 18 eV is shown in Figure 2 in order to illustrate the detection technique. As the ion detection is tuned for "zero" energy ions, only narrow peaks are obtained whenever such ions are produced, i.e. whenever DEA has a finite CS at the threshold. The first peak is at about 4 eV and is the process of interest for the present analysis technique. At higher energy there is a series of peaks corresponding to dissociation channels with the H atom in an electronically excited states with  $n=2, 3, 4$ , etc. This series is terminated by the threshold for ion-pair production where the reaction products are H<sup>-</sup>, H<sup>+</sup> and a free electron. This process is not resonant and occurs in a similar way as for electron impact ionisation at any energy above the threshold. The DEA threshold energy for formation of excited H atoms is  $3.72+E_{\text{exc}}$ , so for  $n=2, 3, 4$  is at 13.92 eV, 15.81 eV, 16.47 eV, respectively. The threshold for ion pair production is therefore at 17.32 eV.

The main purpose of the present method is not a spectroscopic study of the hydrogen molecule itself but the determination of vibrational excitation of this molecule. As shown in Figure 2, for cold hydrogen gas, a peak at about 4 eV can be observed. If the gas contains vibrationally excited molecules then new peaks at lower energy are detected. This is due to the fact that the higher the target excitation energy, the lower the threshold for DEA. This is illustrated by the spectrum shown in Figure 3. In this particular instrument, vibrationally hot hydrogen molecules can be formed by surface recombination of atoms in the specially designed gas cell containing an incandescent tungsten filament. Neutral molecules are dissociated on the filament and atoms recombine on the cooled walls of the cell thus forming excited molecules.



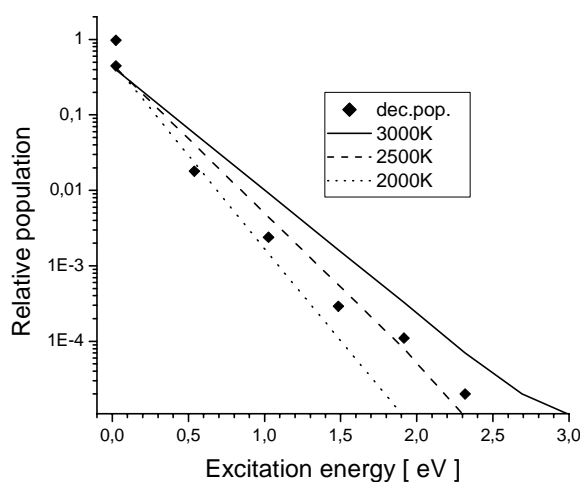
**Figure 2.** H<sup>-</sup> yield as a function of electron energy for a room temperature H<sub>2</sub>. Different DEA processes occur at different energies. DEA at 14eV is the most prominent but for vibrational diagnostics of hydrogen the 4eV process is used.

In Figure 3 we see a series of peaks below the energy of the cold molecule peak and the energy separation of these peaks tells us what state the target molecule was in. Therefore, the peaks are easily identified as being due to  $v=1,2,\dots,6$  vibrationally excited states. The energy scale in spectra presented here is shifted so that the indication of the reaction channel is set at the peak and not at the corresponding threshold as mainly energy differences are important here.



**Figure 3.** H<sup>-</sup> yield as a function of electron energy for 4 eV DEA in H<sub>2</sub>. Two spectra are for a hot (dot and line) and cold (full line) target gas.

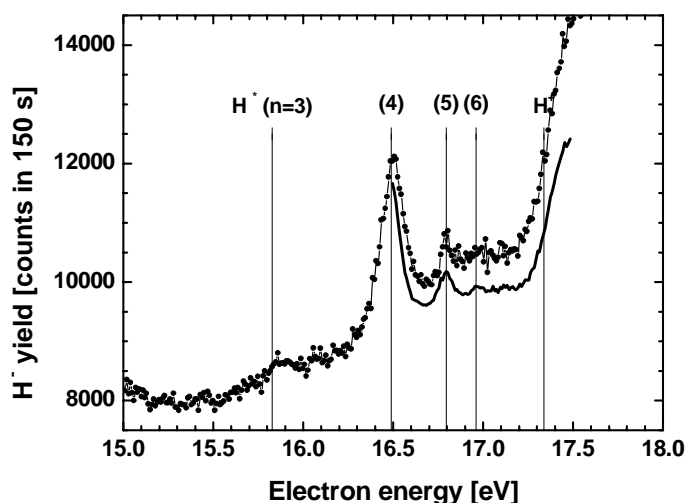
In order to be of practical use such an experimental spectrum must be analysed and the relative populations of excited molecules in the target gas has to be determined. A deconvolution procedure is therefore needed that takes into account the experimental parameters (apparatus function) and characteristics of the CS for DEA. The apparatus function depends on the shape and energy distribution of the electron beam and ion extraction, and detection efficiency. Experimental total<sup>18,19</sup> and differential<sup>4</sup> CS are available as well as the experimentally determined dependence of the DEA CS on ro-vibrational excitation.<sup>7</sup> Besides these experimental data there are numerous theoretical studies of the 4 eV DEA process in H<sub>2</sub> (see references in Ref. 19). By using the experimental peak for a cold gas as apparatus function and the threshold peak values of CS, a simple deconvolution procedure has been developed for spectra analysis and determination of the vibrational state populations. The resulting distribution for the spectrum from Figure 3 is shown in Figure 4. The high sensitivity of this method for excited molecules is due to the very strong increase of the DEA CS with vibrational excitation.



**Figure 4.** Population of vibrational states as deduced from the spectrum of Figure 3 for hot hydrogen (diamonds). The lines indicate Boltzmann populations at the indicated temperatures.

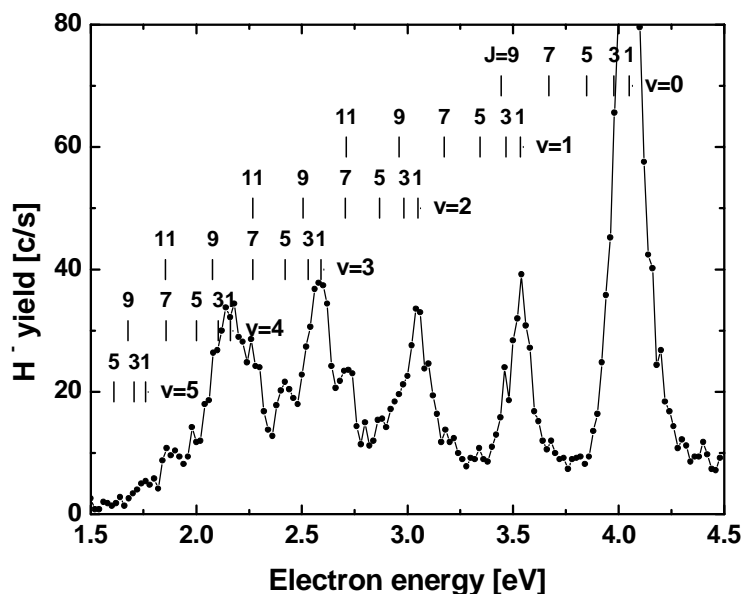
### Examples and discussion

Two spectra with higher statistics of the high-energy DEA processes are shown in Figure 5. These spectra show the important production of  $H^-$  for  $n=4$  but that DEA for  $n=3$  does not produce low energy ions. A series of processes can be observed in Figure 5 up to  $n=6$ . From these characteristics one can deduce the properties of the potential curves for the series of resonant states in the Franck-Condon region of the ground state. Measurements with a hot target gas revealed no strong dependence of any DEA channel on vibrational excitation apart from the 4 eV one.



**Figure 5.** Two spectra of high-energy DEA processes in cold hydrogen collected with higher statistics. Full line represents the spectrum taken with higher statistics and it is approximately normalized to the one represented by the dotted line.

The present method can be efficiently used also for the studies of processes on surfaces. An example of such a study was the influence of a thin evaporated gold film on the vibrational excitation of recombined molecules.<sup>17</sup> In this study two distinct forms of the film were observed, noted as type I and type II, presumably due to the change of the surface morphology and hydrogen content. The transition from type I (freshly evaporated thin film) and to type II was induced by the heating the surface. Both surfaces yielded clean vibrational spectra with different intensities. However, during the short transition period from one surface type to the other, spectra with important rotational excitation were observed. A spectrum at this transition phase is shown in Figure 6. One can observe strong rotational peaks of higher vibrational states indicating interesting phenomena. More studies on time evolution of the spectra are needed in order to understand the underlying processes.

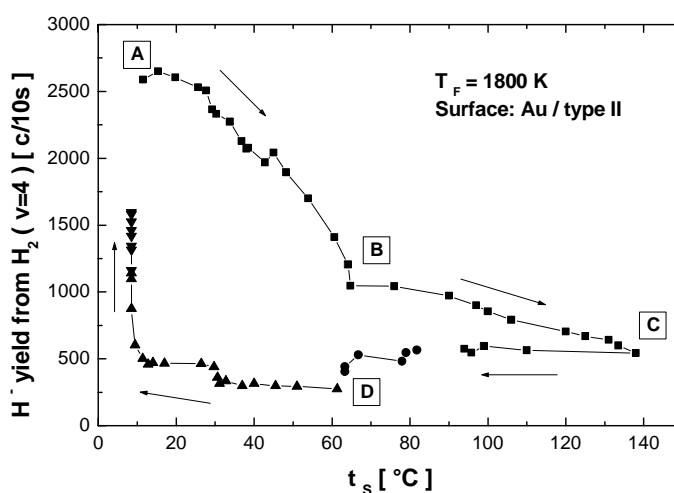


**Figure 6.** Transient  $\text{H}^+$  spectrum during the structural change of an evaporated Au film. During this transition, relatively pronounced rotational excitation is detected contrary to the case when the surface is stabilised. The energies of odd rotational states for each vibrational level are indicated by vertical lines.

Another application of the present method is for the studies of temperature dependence of atomic recombination on the surfaces. The variation of  $v=4$  hydrogen molecule formation with the cell wall temperature, i.e. with the temperature of the



recombination surface is shown in Figure 7. Here, the electron energy is tuned on the  $v=4$  peak and both electron energy and ion detection were kept constant during the measurement. In the A-B section the cell temperature was varied by changing from water to air cooling. At B the air-cooling flow was reduced to a very low value and at C it was increased again. Finally, in D the cooling fluid was changed from air to water. During this experiment the hydrogen flow through the cell as well as the flux of H atoms from the dissociating filament (constant filament temperature) were kept constant. The surface of the cell was an in situ evaporated gold film.

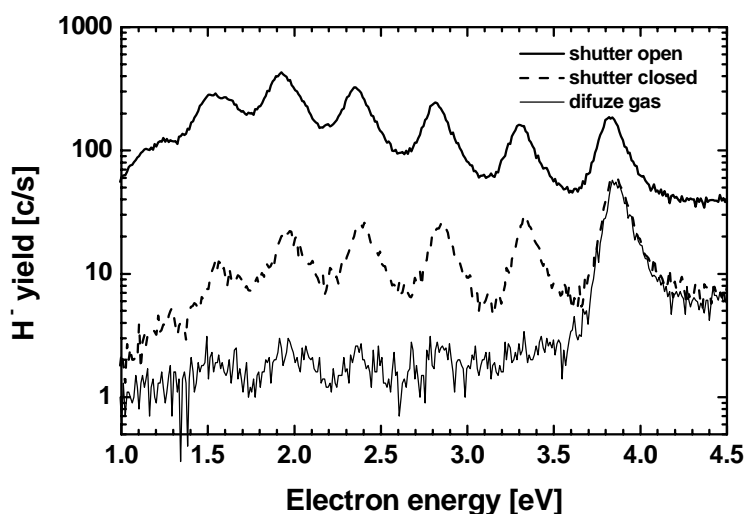


**Figure 7.** Variation of the signal due to  $v=4$   $H_2$  molecules from the excitation cell with the wall temperature.

From this kind of measurement one can get information on the state of the recombining surface and the observed hysteresis indicates the slow restitution of the surface by physisorption and/or diffusion of hydrogen atoms.

A final example is of importance to vacuum science and is shown in Figure 8. The top spectrum corresponds to the normal operation of the hot hydrogen cell. This means that the dissociation filament is on, hydrogen is flowing through the cell and the effusing sample beam is analysed by the above described set-up. Subsequently, keeping the same experimental conditions a large, flat, metallic obstacle is placed between the cell exit orifice and the interaction region. In this way, the molecules leaving the cell could not travel straight to the interaction region, but have to collide many times within the vacuum chamber before arriving there. The middle spectrum of Figure 8 is taken under

such conditions. This spectrum is now characteristic of the background gas in the vacuum cell and one still observes a very important presence of vibrationally excited molecules. This means that such molecules show slow vibrational relaxation on the vacuum chamber walls and once produced in the cell they are present until being pumped out. Finally, the bottom spectrum is taken by keeping the dissociation filament at the same temperature as before but introducing the same flow rate of hydrogen by an auxiliary side port into the vacuum. Even in this situation, the presence of vibrationally excited molecules can be observed as a result of the low pressure background gas present in the cell. This example shows, that with hot filaments one can expect the presence of vibrationally excited hydrogen molecules. This, in turn, may influence vacuum processing if the reaction rates for such molecules are high.



**Figure 8.**  $\text{H}^-$  spectrum for hot hydrogen - top curve, spectrum with obstructed access of hot molecules to the interaction region - middle curve, and spectrum with cell filament on but hydrogen gas being introduced with the same flow rate, as for the above two cases, through an auxiliary port - bottom curve.

## Conclusions

A short review of the use of negative ions for molecular spectroscopy is presented mainly taking as an example the vibrational spectroscopy of the hydrogen molecule. The wide variety of the specific properties of DEA to individual molecules allows development of new methods for particular studies. The method described for vibrational spectroscopy of hydrogen based on DEA is important as it facilitates

unprecedented studies of processes at surfaces and in plasmas. Simultaneous application of this method with more elaborate optical methods<sup>20</sup> would provide detailed new experimental information on the DEA process in hydrogen.

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### Povzetek

Podan je kratek pregled uporabe zajetja elektronov na molekule na področju molekulske spektroskopije. Povdarek je na vibracijski spektroskopiji vodikovih molekul, ki temelji na detektiranju nizkoenergijskih H<sup>+</sup> ionov iz disociativnega zajetja elektronov. Prikazano je nekaj primerov uporabnosti metode.