PHYSICAL REVIEW A VOLUME 52, NUMBER 1 JULY 1995

Enhanced charge transfer to molecular ions by electronic excitation of the target

R. Bruckmeier,* Ch. Wunderlich, and H. Figger
Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany

(Received 15 December 1994)

A beam of molecular ions (ArH^+, ArD^+, or $D_3{}^+$) was neutralized by passage through an excited cesium vapor; two single-mode diode lasers were used to populate the $6\,^2P_{3/2}$ state of the cesium atoms. The charge-transfer cross section could be increased by laser excitation of the Cs target, in some cases by orders of magnitude. This was established by observing the intensity of the luminescence from the neutralized molecules, which was enhanced by a factor of up to 10. The enhancement factors are in qualitative agreement with results of computations that follow the theoretical treatment for atoms introduced by Rapp and Francis [J. Chem. Phys. **37**, 2631 (1962)]. This experimental technique is a generally applicable method for any molecular-beam technique that relies on charge transfer.

PACS number(s): 34.70.+e, 34.80.Qb, 33.20.Kf, 33.20.Lg

I. INTRODUCTION

Charge-transfer processes are among the most fundamental and frequent processes encountered in nature. For example, oxidation (and its counterpart reduction) is, in its general sense, a charge-transfer process. Charge transfer can, in many cases, be induced or influenced by light impinging on the material under investigation. Subjects of current research are, e.g., in biology the photosynthesis of chlorophyll, or in solid-state physics the solar cell; in both processes the absorbed light separates charges producing "free" electrons and holes followed by charge-transfer processes between donors and acceptors [1].

Elementary chemical gas phase reactions with very large (100 Å^2 and more) cross sections, e.g., $Li+F_2 \rightarrow LiF+F$, are also explained in terms of a charge-transfer mechanism: the valence electron of the lithium atom attaches itself to F_2 and by ionic attraction $Li^+F_2{}^-$ is formed; in a final step, one F atom is expelled from this intermediate complex [2]. Experiments on charge transfer to atomic ions in the gas phase have some similarity to this class of reactions. These experiments have mostly been performed using crossed beams (in some cases the charge donor was electronically excited by light), and in most cases alkali atoms have been employed to transfer their valence electron to some atomic ion. In these experiments, the alkali atoms were excited by the light of dye lasers [3] or, in the case of rubidium and cesium, by diode lasers [4]. Usually, the effect of exciting the electron of the donator is to reduce the difference between the ionization energies of the electron donator and the acceptor. The remaining gap between the ionization energies ΔE can be bridged by the suitable Fourier component of the electric field that is generated when the atoms (or molecules) participating in the charge transfer pass each other. Massey [5] pointed out that the matching Fourier component is at its maximum when the following relation is fulfilled:

$$\frac{\Delta E}{h}=\frac{v}{a}\,, \tag{1}$$

where v stands for the relative velocity of the charge-transfer partners, and a is a length of atomic dimensions. A more detailed quantum-mechanical theory was invoked by Rapp and Francis [6] who solved the time-dependent Schrödinger equation employing hydrogenlike $1s$ electronic wave functions to calculate charge-transfer cross sections. Their work has been improved and corrected several times, see, e.g., [7–9]. Orientational and spin effects have not been considered in these treatments of which the main qualitative results are for $\Delta E=0$ (resonant charge transfer), the cross section $\sigma(v)$ decreases monotonically when the relative velocity v of the charge-transfer partners ranges from 10^2 to 10^8 m/s. For $\Delta E\neq 0$ (nonresonant transfer), $\sigma(v)$ increases with increasing velocity v until the so-called Massey criterion [Eq. (1)] is fulfilled. At this velocity, $\sigma(v)$ reaches its maximum, which is close to the cross section one would obtain if ΔE was equal to zero. Then $\sigma(v)$ decreases monotonically with further increasing velocity v and approaches the curve describing resonant charge transfer. A comparison of the calculated cross sections with experimental results using identical (i.e., $\Delta E=0$) and different (i.e., $\Delta E\neq 0$) collision partners reported in Rapp and Francis' work furnished qualitative agreement.

Surprisingly few experiments have been performed so far on charge transfer using an electronically excited target. Kushawaha [3] neutralized a beam of H^+ by directing it into a sodium cell. Through a side window of the cell, Lyman-α radiation emitted by excited hydrogen atoms was observed and used as a measure for the charge-transfer cross section of the reaction $H^+ + Na \rightarrow H^* + Na^+$. When the sodium atoms were ex-

---

*Present address: Universität Konstanz, Postfach 5560/M696, 78434 Konstanz, Germany.

1050-2947/95/52(1)/334(8)/$06.00

cited to the $3p$ state using a dye laser collinear with the ion beam, an enhancement of the Lyman-α radiation of up to 90% was observed. The relative cross sections with and without excitation of the sodium atoms, σ_p and σ_s (i.e., the valence electron being in the $3p$ state or in the ground state) was measured as a function of the H^+ velocity and found to be in qualitative agreement with the theory of Rapp and Francis. In a similar experiment, Finck *et al.* [4] crossed a beam of H^+ that was accelerated to energies between 0.5 and 10 keV with a thermal Na beam. They obtained quantitative agreement with theory for the cross-section ratio σ_p/σ_s. In that experiment, the orbital alignment of the alkali-atom target was controlled by the use of polarized light to excite the Na atoms. A number of similar experiments have been performed, e.g., Royer *et al.* [10] took advantage of the time-of-flight (TOF) method to analyze with high precision the translational energy of neutralized H atoms produced in the reaction $H^+ + Na \rightarrow H^* + Na^+$, which allowed them to identify all of the outgoing channels of this reaction.

Very recently, He^{2+} was used as a projectile by different experimenters using oriented alkali-atom targets: Gieler *et al.* [11] investigated the charge transfer during the reaction $He^{2+} + Na(3s,3p) \rightarrow He^+(n=2,3,4,5) + Na^+$. They, too, analyzed the translational energy of He^+ after the charge transfer took place. In Ref. [12], experiments are reported where, besides Na, Li was used as a target. The results have been compared with a 64-state atomic-orbital close-coupling calculation which could reproduce the experimentally observed dependence on the Na* and Li* orientation. The experiments of Schlatmann *et al.* [13] also showed a strong dependence of the transfer cross section on the alignment of the target. In particular, they could establish a correlation between the charge-transfer cross section and the relative velocity of the projectile and the electron in the target atom. This was also shown by Houver *et al.* [14] for the target electron in circular states excited by circularly polarized light: a strong left-right asymmetry has been observed for the scattered H atoms when the velocity of the projectile matched the classical velocity of the orbiting target electron.

So far, charge transfer from an electronically excited target to molecules seem to have been studied very rarely. Banares *et al.* [15,16] began to study the charge-transfer reaction $Na(3P_{1/2,3/2}) + I_2 \rightarrow Na^+ + I_2^-$ by crossing a beam of dye laser excited Na with a supersonic I_2 beam. Measuring the yield of I_2^- ions made it possible to determine the electron affinity of I_2 as well as the threshold energy for this reaction for both spin orbit states of Na. Salgado *et al.* [18] used H_2^+ as a projectile and Na as a target, which they aligned making use of polarized laser light. They studied the charge transfer to different H_2 states by measuring the translational energy of H_2 molecules applying a TOF method, similar to the experiment on H^+ mentioned before [14].

In the work presented here, a beam of ArH^+, ArD^+, or D_3^+ accelerated to an energy of 15 keV was crossed with a cesium atomic beam, and part of the Cs atoms were excited by the linearly polarized light of two single-mode, 852-nm diode lasers. Having passed the Cs cell, a neutral molecular beam of excited ArH, ArD, or D_3 emerged which emitted characteristic rovibronic band spectra, since the electron was transferred into excited orbitals that then decayed to lower-lying states. ArH, ArD, and D_3 are excimer molecules of the Rydberg type whose structure can roughly be described by a simple model where a valence electron is orbiting around a molecular ionic core. The energy gap ΔE between the ionization energies of Cs and the neutralized molecules was decreased by the energy of one ir photon (1.45 eV) when the Cs atoms were excited.

By excitation of the Cs atomic target, an increase in emission intensity by a factor of greater than 10 could be achieved in the case of the $E\,^2\Pi \rightarrow A\,^2\Sigma^+$ band of ArD. The intensity of the corresponding band of ArH became strong enough to emerge from the noise only after excitation of the Cs atoms. Thus, the application of this technique decidedly improved the signal-to-noise ratio of the recorded spectra and, in the case of ArH, made it possible to measure a complete band of this molecule using a molecular-beam technique.

Similar experiments were performed using D_3^+ as a projectile, and the uv spectra of D_3 were investigated with and without excitation of the Cs target. An increase of the intensity by a factor of 2.0 was observed in this case.

In the experiments reported here, the molecules serving as projectiles were not oriented prior to the charge transfer, which however, should be possible since, e.g., ArH and ArD possess a permanent electric-dipole moment. So far, to our knowledge, no experiment with oriented target and oriented projectile molecules has been performed.

In addition to reporting experimental results on the charge transfer between different molecular ions and Cs atoms in Sec. II, the dependence of the transfer cross section on ΔE will be compared with computational results obtained by following the theoretical treatment of Rapp and Francis [6], which will be briefly outlined in Sec. III.

II. EXPERIMENT

A. Experimental setup

A schematic drawing of the experimental setup is shown in Fig. 1. The main components, with the exception of the diode laser setup have been described before [17]. Therefore, only a summary will be given here: positive molecular ions were formed in a duoplasmatron where a dc discharge was run through a gaseous mixture of the constituents (i.e., Ar and H_2 or D_2) of the molecules to be investigated. An ion beam was extracted from this source, accelerated to 15 keV, and then collimated with the help of an Einzel lens, and mass selected in a sector magnetic field. The ion current was typically 40 μA of D_3^+ and 20 μA of ArH^+ and ArD^+. After having traversed a second ion lens system, which served to collimate the ion beam, it crossed a thermal cesium atomic

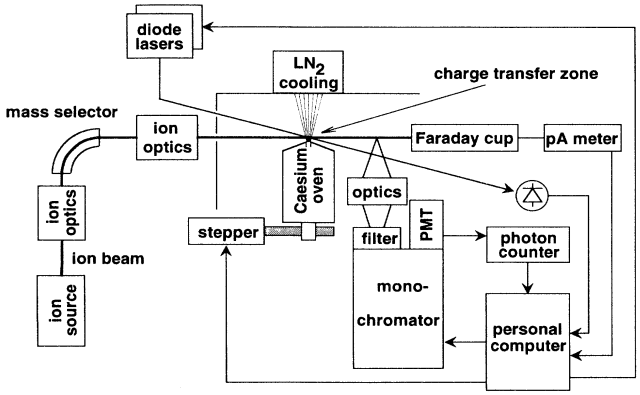

FIG. 1. Schematic overview over the experimental setup: a fast beam (15 keV) of molecular ions is neutralized in laser-excited alkali-atom vapor. The luminescence of the neutral molecules is monitored by means of photon counting. LN$_2$ denotes liquid nitrogen.

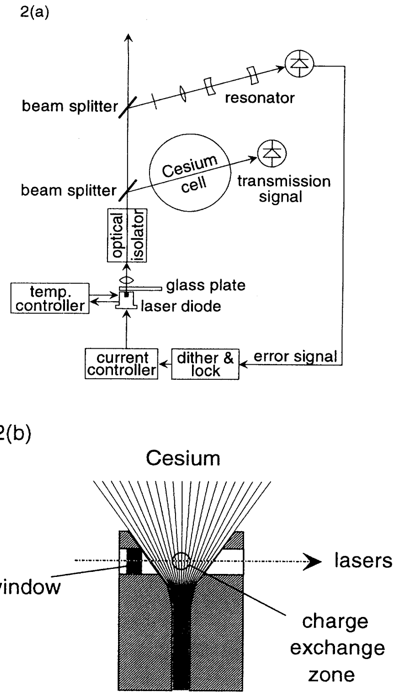

FIG. 2. (a) Setup of the diode lasers. (b) Vertical cut through the head of the Cs oven. The region where the molecular beam (intersecting the laser beam at an angle of approximately 45°) passes through the alkali vapor is indicated by a circle (charge-transfer zone).

beam emerging from an oven that was temperature stabilized to maintain a temperature of typically 200 °C. Here, about 50% of the molecular ions were neutralized. The remaining ion current was measured employing a Faraday cup and a pA meter. The photons emitted by the well collimated, mono-energetic (15 keV) beam of neutral excimer molecules were collected by a system of broadband mirrors which focused the light onto the entrance slit of a 1.5-m monochromator made by Yobin-Ivon. Laser-induced fluorescence at the excitation wavelength of Cs was prevented from entering the monochromator by an appropriate interference filter. The signal of a Burle C31034 photomultiplier tube that detected the photons at the exit slit of the monochromator was sent to a photon counter and then to a personal computer. The computer controlled the movement of the grating and thus the wavelength transmitted by the monochromator as well as the position of the Cs oven (i.e., the charge-transfer zone) relative to the point where the light emitted from the molecular beam was collected. This allowed us to determine lifetimes of the emitting neutralized species by measuring the decay of the fluorescence along the molecular beam [17].

Two multiquantum well laser diodes of the type LT50-A-3U made by STC Optical devices were used for the excitation of the Cs atomic beam. The setup is shown in Fig. 2. The heat sink of the diode laser was temperature stabilized keeping fluctuations below 1 mK. A glass plate was mounted a few tenths of a millimeter away from the beam exit of the diode. Varying the distance between the plate and the diode with the help of a piezo crystal made the laser hop through different longitudinal modes thereby allowing coarse tuning, that could be controlled by directing the laser light to a wave meter or through a Cs cell. Fine tuning and scans around the Cs resonances were achieved by variation of the diode current. The laser wavelength was locked to a temperature stabilized confocal interferometer. Thus, changing the resonance wavelength of the interferometer allowed fine tuning of the laser. This was accomplished by making use of a piezo-electric crystal to move one of the end mirrors. The output power of the diodes running at wavelengths (around 852.3 nm) suitable to excite the $F=3$ and $F=4$ hyperfine levels of the $6s\,^2S_{1/2}$ ground state to the $F=2,3,4,5$ hyperfine levels of the $6p\,^2P_{3/2}$ state was approximately 40 mW and the spectral width (full width at half maximum) about 14 MHz. Single hyperfine levels of the excited $P_{3/2}$ state could not be resolved due to Doppler broadening, which amounts to 470 MHz at 190 °C. The laser beams were focused to a spot of approximately 80 μm in diameter resulting in a peak intensity of several hundred W/cm^2. The Cs beam (density about 10^{14} cm^{-3}) emerging from the oven was much larger in diameter [approximately 3 mm, compare Fig. 2(b)] and only a small fraction of the Cs atoms were excited directly by the unshifted laser light. Since the intensity in the laser beam was far beyond what was necessary to saturate the atomic transition, the light intensity decayed linearly instead of exponentially when traveling through the Cs beam. Cs atoms not directly exposed to the laser beam could be excited by Doppler shifted light (diffusing through the Cs beam) whose intensity amounts to a few W/cm^2 and, therefore, is still orders of magnitude larger than the saturation intensity of the Cs transition in question. This made it possible to excite not just a small velocity class (corresponding to the relatively narrow bandwidth of the lasers) out of a broad Doppler profile. Atoms at the edges of the Cs beam, however, possibly did not experience an intensity high enough to drive them into saturation.

Finck *et al.* [4] employed a laser intensity of 30 mW/cm^2 to drive the $3s\ ^2S_{1/2} \rightarrow 3p\ ^2P_{3/2}$ transition in sodium and arrived at a fractional number α of excited atoms between 0.13 and 0.18. For the reasons mentioned before, the fraction of excited Cs atoms interacting with molecular ions is quite large and a reasonable estimate is $\alpha = 0.35$ for the experiments reported here.

Two lasers were used to excite both the $F = 3$ and the $F = 4$ hyperfine structure component of the ground state to avoid optical pumping between these levels. However, it turned out that effects of optical pumping did not play an important role: using two lasers (one each for the $F = 3$ and $F = 4$ levels) resulted in an increase of the gain of the measured signal from the $E\ ^2\Pi$ level of ArD (see below) of only 30% as compared to making use of just one of the two lasers. This indicates that the hyperfine levels were probably mixed by collisional processes. The fact that the increase in intensity of the luminescence from ArD was much smaller than expected when doubling the laser intensity, shows that the Cs vapor near the charge-exchange zone was not far from saturation ($\alpha = 0.5$).

B. Experimental results

In order to determine the change in the cross section for charge transfer to a given molecular electronic state when the electron donor Cs was excited, the monochromator was set to a wavelength corresponding to the transition from the molecular level in question to some lower state. When investigating D_3 it was set to transmit light of 312 nm originating from the transition $3s, 3d \rightarrow 2p\ ^2E'$ which gives rise to a continuous, bimodal uv spectrum with one maximum located around 312 nm and the other around 235 nm [21]. The count rate due to the luminescent light at 312 nm was measured when the diode lasers were tuned and focused such that the maximum possible count rate was detected. Then the lasers were blocked and the count rate was measured again; finally the number of background counts per second was determined when both the lasers, and the ion beam were blocked. This "manual" boxcar technique furnished the data displayed in Fig. 3(a) from which the enhancement factor β_i of the charge-transfer cross section could be extracted (i stands for a particular molecular electronic state). A factor $\beta_{n=3} = 2.0$ was reached for the $n = 3$ levels of D_3 which mainly contribute to the emission around 312 nm. This result is consistent with the outcome of Fukuda's work who also arrived at an enhancement factor of 2 by employing a ring dye laser with 100-mW output power [22,23]. In this case, bands in the visible originating from the $n = 3$ levels were investigated.

In the electron transfer process no stable (against predissociation) electronic states other than $E\ ^2\Pi$ and $B\ ^2\Pi$ of ArH and ArD seem to be populated, since the bands due to the transitions $E\ ^2\Pi \rightarrow A\ ^2\Sigma^+$, $E\ ^2\Pi \rightarrow X\ ^2\Sigma^+$, and $B\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ are the ones that have been detected. Figure 3(b) shows the effect of laser excitation when monitoring the $B\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ transition at 312 nm in ArD. In this case, an enhancement factor of 4.9 was obtained. The signal from the Q branch of the $E\ ^2\Pi \rightarrow A\ ^2\Sigma^+$ transition in ArD is amplified by a factor of 10 as can be seen in Fig. 3(c). This, to our knowledge, is the largest enhancement factor attained so far by laser excitation of the electron donor in a charge-transfer process.

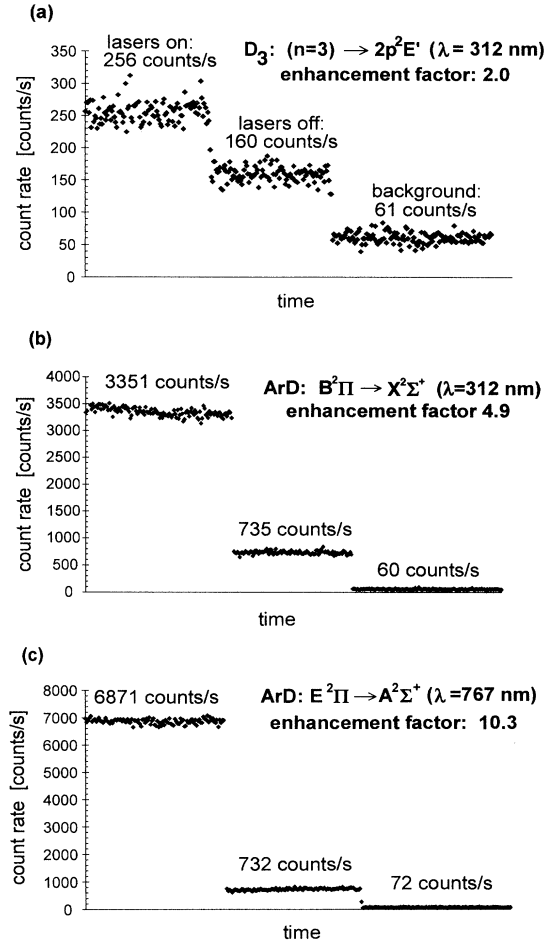

FIG. 3. Measurement of the enhancement of the charge-transfer cross section to the (a) $n = 3$ levels of D_3; (b) $B\ ^2\Pi$ state of ArD; (c) $E\ ^2\Pi$ state of ArD.

These experimental results are summarized and compared with theoretical predictions (which were reached by applying the treatment outlined in the following section) in Fig. 4. The theory of Rapp and Francis [6] tailored to our experimental situation predicts an enhancement factor of 1.0 and 1.1 for charge transfer to the $3d$ and $3s$ levels, the main emitters of the uv radiation [21] of D_3 when Cs is excited to the $6p\ ^2P_{3/2}$ level. This has to be compared with the measured factor of 2.0. In the case of ArD (or ArH) the charge transfer to the $B\ ^2\Pi$ state and, therefore, the intensity of the measured luminescence in the uv should increase by a factor 3.7 according to theory, which agrees fairly well with the measured value of 4.9. Calculations yield a factor of 17 for

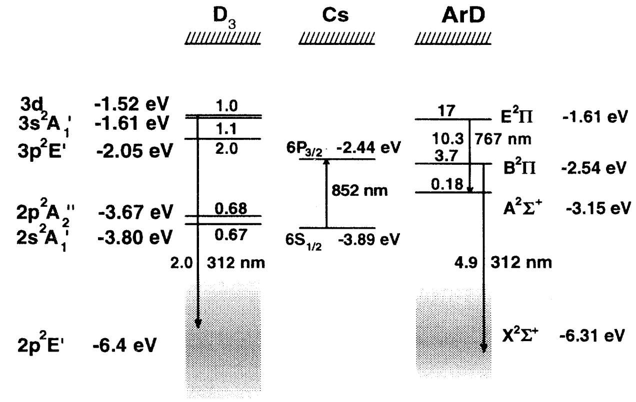

FIG. 4. Term diagram of relevant electronic states of the molecules under study and the charge-transfer partner Cs. The number above each molecular level is the calculated factor by which the charge transfer from Cs to the corresponding molecular ion is enhanced when a fraction $\alpha=0.35$ of the Cs atoms is excited to the $6p\,^2P_{3/2}$ level. The arrows pointing downward indicate the investigated transitions and the numbers next to them are the experimentally observed enhancement factors for the upper level.

the raise in population of the $E\,^2\Pi$ state of ArD. The value observed in the experiment was 10.3 in this case. Considering the approximations of the theoretical approach used here, the agreement of experiment and theory is fair.

In addition to the measurement of the enhancement factors, the complete bands of ArD and ArH around 767 nm ($E\,^2\Pi \rightarrow A\,^2\Sigma^+$ transition: Johns' band) were recorded with excitation of the charge-transfer medium. The results are shown in Fig. 5 and Fig. 6. These bands were first observed by Johns in a rf discharge [24] and later in a Cossart-type plasma beam tube [25] where also laser spectroscopy on these Rydberg molecules became feasible [26]. Lifetimes of individual rotational levels of the emitting state of this band ($E\,^2\Pi$) have been measured by Wunderlich *et al.* [17] who also recorded the band of ArD around 767 nm that could be investigated employing the technique described above that does not rely on spectroscopy of a gas discharge. By excitation of the charge-transfer medium, the signal-to-noise ratio of these spectra was improved considerably and many lines not observed before with a molecular-beam method emerged from the noise (e.g., all the lines of the $v''=1 \rightarrow v'=1$ band of ArD). This is particularly striking in the case of the ArH band displayed in Figs. 6(a) and 6(b) where the *P* branch and *R* branch become visible only after excitation of the electron donor Cs.

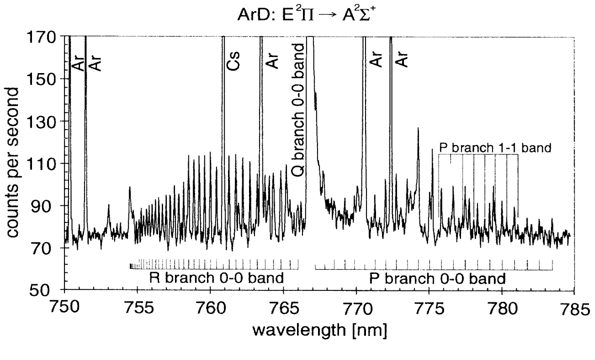

FIG. 5. Spectrum of ArD around 767 nm (Johns' band) obtained with diode laser excitation of the charge-transfer medium cesium. The gain in intensity of the molecular lines was a factor of 10 [measured using the *Q* branch, see Fig. 3(c)] when Cs was excited to the $6p\,^2P_{3/2}$ level. Many of the lines of the *P* and *R* branch of the $v''=v'=0$ transition and all the visible lines of the $v''=v'=1$ transition emerged from the "noise" only after excitation of the electron donor Cs.

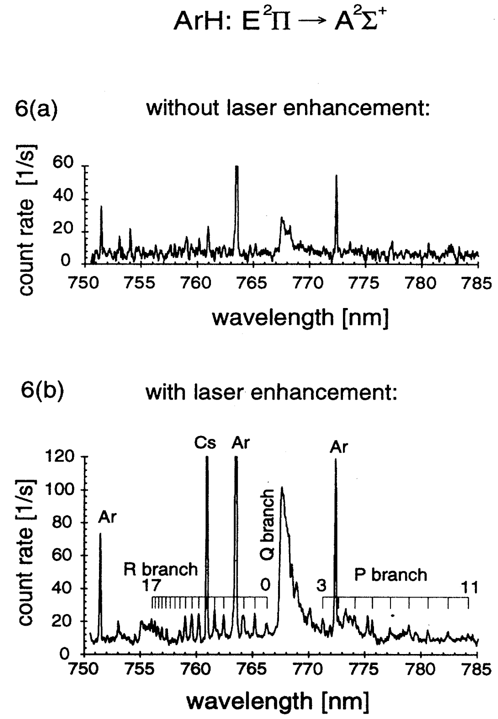

FIG. 6. Spectrum of ArH around 768 nm (Johns' band): (a) Cs in its ground state was used as a charge-transfer partner. Only the *Q* branch of the $v''=v'=0$ band could be identified. (b) The Cs atoms were excited by diode lasers while this spectrum was recorded. The *R* and *P* branch of this band can now clearly be identified.

III. CALCULATIONS AND DISCUSSION

In our calculation of the charge-transfer cross section, we followed closely the theoretical treatment of Rapp and Francis [6] and, therefore, only a brief outline of this theory will be given below. This relatively simple quantum-mechanical approach allows one to calculate the cross section for charge transfer as a function of the relative velocity *v* of both charge-transfer partners and of the ionization potentials *I* of the atoms (or molecules) involved.

The wave function ψ of the electron during the nonresonant reaction

$$(A^+ + e^-) + B^+ \rightarrow A^+ + (B^+ + e^-)$$

is approximated by a linear combination of ϕ_A and ϕ_B:

$$\psi = c_A(t)\phi_A \exp(-i\omega_A t) + c_B(t)\phi_B \exp(-i\omega_B t) ,$$

where $\phi_j(r_j)$ stands for an atomic wave function of the form

$$\phi_j(r_j) = N \exp\left[-\gamma_j \frac{r_j}{a_0}\right], \quad j \in \{A, B\} ,$$

describing the electron in a 1s-like orbital bound by a potential V_j either to the ionic core A^+ with ionization energy I_A or to B^+ with ionization energy I_B [$\gamma_j \equiv (I_j/13.6 \text{ eV})^{1/2}$, r_j represents the distance between the electron and the respective positive core, N is a normalization constant, and $\omega_j \equiv I_j/\hbar$]. Inserting this linear combination ψ into the time-dependent Schrödinger equation leads to two coupled differential equations for the coefficients $c_A(t)$ and $c_B(t)$,

$$\begin{aligned} i\dot{c}_B &= \kappa_1 \exp(i\omega t) c_A + \eta_1 c_B , \\ i\dot{c}_A &= \eta_2 c_A + \kappa_2 \exp(-i\omega t) c_B , \end{aligned} \tag{2}$$

with $\omega \equiv \omega_B - \omega_A$ (see also the appendix). Initially, the electron is bound to the target atomic core A^+ and the initial conditions $c_A(-\infty)=1$ and $c_B(-\infty)=0$ hold. The probability $P(b,v)$ (b is the impact parameter) for finding the electron bound to B^+ after the interaction between the charge-transfer partners, is then given by $|c_B(\infty)|^2$ and has been obtained from Eqs. (2) by numerical integration. In this work, no further approximations were used when solving Eqs. (2) for c_A and c_B. The cross section for charge transfer, σ can then be calculated by integrating $P(b,v)2\pi b$ over b. All computations were performed on a personal computer (486 CPU).

The goal of the experiments reported here was to increase the population of particular molecular states by exciting the target Cs atoms from the $6s\,{}^2S_{1/2}$ to the $6p\,{}^2P_{3/2}$ state. Numerical results obtained from the computational approach outlined above will be presented in what follows.

In Table I, the cross sections computed for the case of charge transfer between Cs and ArD$^+$ (accelerated to a velocity v that corresponds to an energy of 15 keV) for all known electronic states [19] are listed. Two values are given for each molecular electronic state: in the last column the cross sections $\sigma_{6S,i}$ for charge transfer from ground state Cs ($6s\,{}^2S_{1/2}$) atoms are tabulated, and the column before lists the cross sections $\sigma_{6P,i}$ involving excited Cs ($6p\,{}^2P_{3/2}$).

With α representing the probability for finding an excited Cs atom in the alkali-atom vapor, the average charge-transfer cross section $\bar{\sigma}_i$ to molecular state i can be expressed as

$$\bar{\sigma}_i(\alpha) = d_i[\alpha\sigma_{6P,i} + (1-\alpha)\sigma_{6S,i}] ,$$

where d_i stands for the degree of degeneracy of molecular state i. The probability W_i for populating molecular state i during the charge-transfer reaction is then given by $W_i(\alpha) = \bar{\sigma}_i/\Sigma_j\bar{\sigma}_j$, where the summation has to be carried out over all molecular electronic states j. When exciting the Cs atoms, charge transfer to the molecular states under study is enhanced by a factor β_i which can be expressed as $\beta_i = W_i(\alpha)/W_i(\alpha=0)$. Making use of the computational results compiled in Table I, the enhancement factors β_i for individual electronic states of ArD have been computed for various values of α and are listed in Table II.

The cross sections and expected enhancement factors relevant for some electronic states of D_3 are listed in Table III. At a higher relative velocity, a larger gap between the ionization energies of the charge-transfer partners is permissible according to the Massey criterion [Eq. (1)]. The charge transfer from ground-state Cs atoms to molecular states of D_3 is, therefore, already quite efficient at the much higher velocity of the $D_3{}^+$ beam (as compared to the ArD$^+$ beam; both were accelerated to 15 keV, and the excitation of Cs leads to only a small increase in the charge-transfer cross section. Thus the weaker dependence of the enhancement factors

TABLE I. Calculated cross sections for charge transfer from ground state ($6s\,{}^2S_{1/2}$, last column) and from excited ($6p\,{}^2P_{3/2}$, fourth column) Cs atoms to the lowest-lying electronic states i of ArD$^+$. d_i represents the degree of degeneracy of electronic state i; I_i is the ionization energy (data on the electronic structure of ArD is taken from Ref. [19]).

ArD state i	$-I_i$ (eV)	d_i	$\sigma_{6P,i}$ (units of a_0^2)	$\sigma_{6S,i}$ (units of a_0^2)
$X\,{}^2\Sigma^+$	6.41	1	0.012	0.49
$A\,{}^2\Sigma^+$	3.15	1	81	77
$B\,{}^2\Pi$	2.50	2	400	6.7
$C\,{}^2\Sigma^+$	2.48	1	400	6.2
$D\,{}^2\Sigma^+$	1.58	1	33	0.12
$E\,{}^2\Pi$	1.53	2	26	0.096
$1^2\Delta$	1.41	2	14	0.065
$F\,{}^2\Sigma^+$	1.35	1	9.8	0.057
$G\,{}^2\Pi$	1.19	2	3.9	
$6\,{}^2\Sigma^+$	1.17	1	3.5	

TABLE II. Calculated factors of enhancement of the charge-transfer cross section for ArD when the electron donor Cs is excited to the $6p\ ^2P_{3/2}$ level. α represents the fractional number of excited Cs atoms encountered by the molecular ions.

ArD state i	$\beta_i(\alpha=0.02)$	$\beta_i(\alpha=0.10)$	$\beta_i(\alpha=0.20)$	$\beta_i(\alpha=0.35)$	$\beta_i(\alpha=0.50)$
$X\,^2\Sigma^+$	0.77	0.39	0.22	0.12	0.067
$A\,^2\Sigma^+$	0.79	0.43	0.27	0.18	0.13
$B\,^2\Pi$	1.7	2.9	3.4	3.7	3.9
$C\,^2\Sigma^+$	1.8	3.1	3.7	4.1	4.3
$D\,^2\Sigma^+$	5.1	12	15	17	18
$E\,^2\Pi$	5	12	15	17	18
$I\,^2\Delta$	4.1	9.3	12	13	14
$F\,^2\Sigma^+$	3.5	7.8	9.6	11	11

β_i on α is comprehensible.

The theoretical treatment outlined above approximates the real charge-transfer process by including into the computations only one molecular electronic state at a time. The charge-transfer cross sections have been computed for those electronic states for which data from *ab initio* calculations were available [19,20]. These encompass all the relevant states that have been observed in the experiment. Emission from higher-lying states was not present in the experiments and neglecting these states in the calculations is justified. Approximating the true wave functions by simple 1*s* orbitals is adequate in this treatment since the charge-transfer probability $P(b,v)$ oscillates rapidly as a function of b for small values of the impact parameter b and is replaced by an average value when evaluating the charge-transfer cross section by integrating $P(b,v)2\pi b$ over b (for details see Ref. [6]). For large impact parameter b (which means large r_j), the approximately exponentially decaying behavior of any possible wave function dominates, and, therefore, the coupling between the electronic states of the donor and acceptor is in good approximation independent of the particular behavior of the wave functions at small b (i.e., small τ_j).

IV. CONCLUSION

The experimental technique relying on the neutralization of a fast molecular ion beam has been appreciably improved by exciting the charge donor and becomes applicable to species of molecules that could not be studied before with this technique as was shown in the case of ArH. The method has become much easier to apply since laser diodes are inexpensive and readily available at wavelengths suitable to excite, e.g., the alkali metals cesium and rubidium. Optical pumping of the electron donor seems not to be critical when high atomic densities are used, which means that only one laser tuned to any of the hyperfine transitions gives sufficient results.

Rb atoms can be highly excited in two steps with two diode lasers working at about 780 and 784 nm. Therefore, it might be feasible to populate molecular levels very close to the ionization boundary by charge transfer.

Not exploited so far in our experiment was the possibility to study alignment effects of the projectiles as well as of the target, though the molecular ions that have been investigated as well as the alkali-atom partner seem to be suitable candidates for such an experiment.

ACKNOWLEDGMENTS

Christoph Kreutner set up the diode lasers and significantly contributed to the first successful demonstration of the technique described here. We thank T. W. Hänsch and A. Weiss for stimulating discussions and would like to acknowledge the indispensable help of W. Simon and H. Brückner in technical matters.

TABLE III. Calculated cross sections for charge transfer from ground state and excited Cs atoms to D_3^+. The last three columns show enhancement factors of the charge-transfer cross section for D_3 when the electron donor Cs is excited to the $6p\ ^2P_{3/2}$ level. Again, α represents the fractional number of excited Cs atoms encountered by the molecular ions.

D_3 state i	$-I_i$ (eV)	d_i	$\sigma_{6P,i}$ (units of a_0^2)	$\sigma_{6S,i}$ (units of a_0^2)	$\beta_i(\alpha=0.10)$	$\beta_i(\alpha=0.35)$	$\beta_i(\alpha=0.50)$
$2p\,^2E'$	6.40	2	0.013	33	0.90	0.65	0.50
$2s\,^2A_1'$	3.80	1	7.2	170	0.90	0.67	0.52
$2p\,^2A_2''$	3.7	1	11	170	0.91	0.67	0.53
$3p\,^2E'$	2.07	2	260	66	1.3	2.0	2.5
$3s\,^2A_1'$	1.62	1	41	32	1.0	1.1	1.1
$3p\,^2A_2''$	1.60	1	37	31	1.0	1.1	1.1
$3d\,^2E'$	1.56	2	30	29	1.0	1.0	1.0
$3d\,^2E''$	1.52	2	24	27	0.99	0.96	0.95
$3d\,^2A_1'$	1.51	1	23	27	0.99	0.95	0.93

APPENDIX

The coefficients $\kappa_{1,2}$ and $\eta_{1,2}$ [Eq. (2)] read as follows:

$$\kappa_1 \equiv \frac{(V_B)_{BA} - F(V_B)_{AA}}{(1-F^2)\hbar}, \quad \kappa_2 \equiv \frac{(V_A)_{AB} - F(V_A)_{BB}}{(1-F^2)\hbar},$$

$$\eta_1 \equiv \frac{(V_A)_{BB} - F(V_A)_{BA}}{(1-F^2)\hbar}, \quad \eta_2 \equiv \frac{(V_B)_{AA} - F(V_B)_{AB}}{(1-F^2)\hbar},$$

where $(V_j)_{ik}$ stands for an integral of the form $\int \phi_i V_j \phi_k$ with $i,j,k \in \{A,B\}$, and $F \equiv \int \phi_A \phi_B$. The explicit expressions for the integrals (in atomic units, using $V_j = -1/r_j$) depend on the separation R of the two ionic cores A^+ and B^+ and are given by

$$F = \frac{8(\gamma_A\gamma_B)^{3/2}[(\gamma_A^2 R - 4\gamma_B - \gamma_B^2 R)\gamma_A e^{\gamma_A R} - (\gamma_B^2 R - 4\gamma_A - \gamma_A^2 R)\gamma_B e^{\gamma_B R}]}{e^{(\gamma_A+\gamma_B)R}(\gamma_A+\gamma_B)^3(\gamma_A-\gamma_B)^3 R},$$

$$(V_j)_{jk} = \frac{-4(\gamma_j\gamma_k)^{3/2}[(\gamma_j^2 R - 2\gamma_k - \gamma_k^2 R)e^{\gamma_j R} - 2\gamma_k e^{\gamma_k R}]}{e^{(\gamma_j+\gamma_k)R}(\gamma_j+\gamma_k)^2(\gamma_j-\gamma_k)^2 R}, \quad j \neq k,$$

and

$$(V_j)_{ii} = -\frac{1}{R} + \frac{1+\gamma_i R}{e^{2\gamma_i R}R}, \quad i \neq j.$$

For completeness, two results of our calculations concerning resonant charge transfer (i.e., the charge-transfer partners are a neutral atom A and the corresponding singly charged positive ion A^+) should be mentioned that slightly deviate from the results given in Refs. [6] and [7]:

(i) The difference in energy δE between the eigenstates of the system A_2^+ for large internuclear separations R (Eq. (8) in Ref. [6], Eq. (8) in Ref. [7]) is

$$\delta E = \frac{8}{3} I_A \frac{R}{a_0} \exp\left[-\gamma \frac{R}{a_0}\right],$$

where $\gamma \equiv (I_A/13.6\text{ eV})^{1/2}$, I_A stands for the ionization energy of atom A and a_0 is the Bohr radius.

(ii) The probability $P(b,v)$ for charge transfer is obtained by evaluating the expression $\sin^2(\int_{-\infty}^{+\infty} \delta E/(2\hbar v)dx)$ (Eq. (3) in Ref. [6]) and the correct approximation for the integral is

$$\frac{4}{3}\left[\frac{2\pi}{\gamma_{a_0}}\right]^{1/2}\left[\frac{I_A}{\hbar v}\right] b^{3/2}\left[1+\frac{7a_0}{8\gamma b}+\cdots\right]\exp\left[-\frac{\gamma b}{a_0}\right].$$

[1] E. Eberl, A. Ogrodnik, and M. E. Michel-Beyerle, Phys. Blätter **3**, 215 (1994).

[2] R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University Press, New York, 1987).

[3] V. S. Kushawaha, Z. Phys. A **313**, 155 (1983).

[4] K. Finck, Y. Wang, Z. Roller Lutz, and H. O. Lutz, Phys. Rev. A **38**, 6115 (1988).

[5] H. S. W. Massey, Rep. Progr. Phys. **12**, 248 (1949).

[6] D. Rapp and W. E. Francis, J. Chem. Phys. **37**, 2631 (1962).

[7] D. P. Dewangan, J. Phys. B **6**, L20 (1973).

[8] Shuji Sakabe and Yasukazu Izawa, At. Data Nucl. Data Tables **49**, 257 (1991).

[9] S. Sakabe, Y. Izawa, M. Hashida, and S. Nakai, Phys. Rev. A **45**, 252 (1992).

[10] T. Royer, D. Dowek, J. C. Houver, J. Pommier, and N. Andersen, Z. Phys. D **10**, 45 (1988).

[11] M. Gieler, F. Aumayr, J. Schweinzer, W. Koppensteiner, W. Husinsky, H. P. Winter, K. Lozhkin, and J. P. Hansen, J. Phys. B **26**, 2137 (1993).

[12] M. Gieler, F. Aumayr, M. Weber, H. P. Winter, and J. Schweinzer, J. Phys. B **26**, 2153 (1993).

[13] A. R. Schlatmann, R. Hoekstra, R. Morgenstern, R. E. Olson, and J. Pascale, Phys. Rev. Lett. **71**, 513 (1993).

[14] J. C. Houver, D. Dowek, C. Richter, and N. Andersen, Phys. Rev. Lett. **68**, 162 (1992).

[15] L. Banares, M. G. Velarde, and A. Gonzales Urena, J. Chem. Phys. **95**, 5474 (1991).

[16] L. Banares, S. Skowronek, C. Perdiguero, and A. Gonzales Urena, Laser Chem. **12**, 33 (1992).

[17] C. Wunderlich, V. Betz, R. Bruckmeier, and H. Figger, J. Chem. Phys. **98**, 9362 (1993).

[18] J. Salgado, D. Dowek, J. C. Houver, C. Richter, B. Saubamea, and J. W. Thomsen, J. Phys. B **26**, L353 (1993).

[19] G. Theodorakopoulos and I. D. Petsalakis, Mol. Phys. **71**, 1055 (1990).

[20] I. D. Petsalakis, G. Theodorakopoulos, and X. Wright, J. Chem. Phys. **89**, 6850 (1988).

[21] R. Bruckmeier, Ch. Wunderlich, and H. Figger, Phys. Rev. Lett. **72**, 2550 (1994).

[22] H. Figger, Y. Fukuda, W. Ketterle, and H. Walther, Can. J. Phys. **62**, 1274 (1984).

[23] W. Ketterle, Ph.D. thesis, Ludwig Maximilian University, Munich, 1986 (unpublished).

[24] J. W. C. Johns, J. Mol. Spectrosc. **36**, 488 (1970).

[25] R. H. Lipson, Mol. Phys. **65**, 1217 (1988).

[26] N. Adolph, T. Heinzel, M. Weidenmüller, and H. Figger, Z. Phys. D **24**, 15 (1992).