Selective Excitation of Parabolic Stark States of He I by Proton Impact

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Resonancelike intensity variations of the impact radiation were observed at electric-field anticrossings of $1snl\,^1L$ and ^3L Stark sublevels ($n=5,6,7$; $l\geq 2$), when investigating excitation of helium atoms by 12.5 keV proton impact. The measured signal amplitudes provide strong evidence that the collision process excites the electron selectively to the (n_1,n_2,m) hydrogenic Stark states $(0,n-1,0)$ and $(0,n-2,\pm 1)$, indicating that the electron is promoted along in-saddle sequences of $H_2{}^+$-like molecular orbitals during the final phase of the collision.

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Excited atomic states formed in inelastic atomic collisions are usually superpositions of atomic eigenstates with some degree of coherence. Here we consider coherent excitation of neighboring energy levels with opposite parity and different angular momenta L. An important property of atoms excited to such coherent superposition states is an asymmetry of the electric charge distribution. In particular, for levels with $\Delta L=1$, a suitable coherence parameter is the electric dipole moment of the transient impact-excited state [1]. Such electric dipole moments have been detected for both hydrogen [1–4] and helium atoms [5,6]. In integral measurements, the dipole moments are parallel or antiparallel to the projectile beam and can be determined by investigating the impact radiation as a function of an electric field varied from pointing upstream to downstream. Thereby, the electric dipole moments of the impact-excited states are compared with the electric-field-induced dipole moments of atomic Stark states [6]. In the measurements performed so far, the investigated impact radiation originated from the decay of a multiplet of Stark sublevels and, therefore, gave rise to complex superposition signals. More detailed information is obtained when analyzing the population of single Stark sublevels separately. For impact-excited helium states, such measurements are possible without high-resolution spectroscopic equipment by investigating the effect of electric-field singlet-triplet anticrossings [7] on the impact radiation. A particularly clear situation is encountered when investigating H^+-He collisions. According to Wigner's spin conservation rule, the helium atom can be excited by proton impact to singlet states only [8]. Therefore, as long as mixing of singlet and triplet states is negligible, the spectral lines of the He I triplet system are absent in the radiation spectrum induced by proton impact. However, at an anticrossing, where a singlet and a triplet Stark state become mixed completely due to spin-orbit interaction, a spectral line of the triplet system appears. This intensity increase of the triplet line and the intensity decrease of the corresponding singlet line is proportional to the number of helium atoms excited to the singlet substate of the anticrossing.

In the present work we studied helium atoms excited by 12.5 keV proton impact to states with principal quantum numbers $n=5$, 6, and 7. A proton beam was crossed with a beam of thermal helium atoms effusing from a capillary multichannel plate. An electric field **F** of up to 11 kV/cm pointing upstream ($F<0$) or downstream ($F>0$) with respect to the proton beam was established in the collision volume by applying voltages $-5\leq U_\pm \leq +5$ kV with opposite signs to a pair of tubes (diam=8 mm, spacing between the tubes $d=7$ mm) upstream and downstream of the collision volume. Details of the experimental setup were published earlier [6].

We measured the intensities $I_\lambda(F)$ of the He I spectral lines corresponding to the transitions $1snd\,^1D$-$1s2p\,^1P$ and $1snd\,^3D$-$1s2p\,^3P$ for $n=5$, 6, and 7 as functions of the electric field $-11\lesssim F\lesssim +11$ kV/cm. Since the spectral lines were selected by interference filters with typical bandwidths $\Delta\lambda\sim 10$ nm, the Stark components of the nd-$2p$ transitions as well as the electric-field-induced Stark components of the neighboring singlet or triplet nl-$2p$ transitions with $l\geq 3$ were detected with approximately the same efficiency.

Recordings of $I_\lambda(F)$ for the two spectral lines at $\lambda(1s5d\,^{1,3}D$-$1s2p\,^{1,3}P)=439$ and 403 nm, respectively, are shown in Fig. 1. A surprising feature of these recordings is their pronounced asymmetry with respect to the sign of the electric field. There are four resonancelike intensity variations at electric fields directed upstream. These intensity maxima of the triplet line and the corresponding minima of the singlet line can be attributed to the four $^1\Lambda\times{}^3\Lambda$ anticrossings of the $1s5d$ Stark sublevels (Fig. 2) discussed by Kaiser, Liu, and von Oppen [7]. The resonances at $F=-4.7$, -7.8, and -10.0 kV/cm are due to the anticrossings of the $1s5d\,^1\Pi$ sublevel with the $1s5d\,^3\Delta$, $^3\Pi$, and $^3\Sigma$, respectively. The strongest resonance at $F=-5.7$ kV/cm is due to the $1s5d\,^1\Sigma\times{}^3\Pi$ anticrossing. Surprisingly, these resonances are almost not visible at fields directed downstream. Instead, there are less pronounced intensity variations which can tentatively be ascribed to anticrossings of the $1s5f$ and $1s5g$ configuration (Table I). Similar results were found for $n=6$ and 7.

Besides these resonances at nonzero electric fields, the

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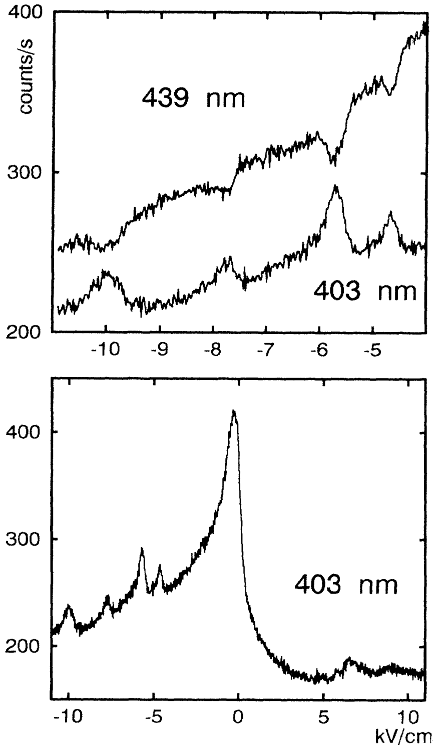

FIG. 1. Recordings of the intensities of the impact radiation at $\lambda = 439$ and 403 nm as a function of the electric field F; above: F pointing upstream (triplet and singlet transition) and below: F scanned from upstream to downstream (triplet transition).

intensity variations around $F = 0$ also contain valuable information about the asymmetry of the electronic charge distribution after the collision process [6]. However, a detailed analysis of these signal structures is elaborate, since the mixing of opposite-parity states caused by the electric field interferes with the demixing of singlet and triplet states [8] due to the same field. Moreover, the intensity variations near zero field are complicated superposition signals with contributions from all Stark sublevels of the $1s5d\,^1D$ level as well as from various cascade processes.

In what follows we shall concentrate on the interpretation and evaluation of the anticrossing signals at nonzero electric fields. The observation that the signal amplitudes are extremely different for $F < 0$ and $F > 0$ indicates that the excitation process is highly selective not only with respect to the spin quantum number S but also with respect to orbital quantum numbers of the excited electron. On the one hand, the Zeeman substates of $1snl$ levels with $\Lambda \leq 1$ are predominantly populated as is well known from polarization measurements on the impact radiation [9]. On the other hand, we infer from our measurements that the impact-excited He I states are almost orthogonal to the $1s5d$ Stark states $|1s5d\,^1\Lambda;F\rangle$ in an electric field pointing downstream, whereas the $1s5d$

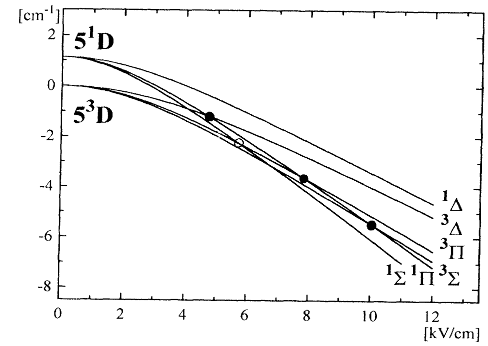

FIG. 2. Electric-field splitting of the $1s5d$ configuration. Term energies as E/hc (cm^{-1}) are plotted vs electric field F (kV/cm). The sublevels are characterized by Stark quantum numbers $\Delta = |M_L|$. The three anticrossings of the $^1\Pi$ sublevel are marked by filled circles and the anticrossing of the $^1\Sigma$ sublevel by an open circle.

Stark states in fields pointing upstream are strongly populated.

The selectivity of the excitation process can be explained by assuming that the excitation of $l \geq 2$ states of He I by 12.5 keV p-He collisions proceeds in two steps: the close encounter and the final phase [6,10]. The excitation mechanism taking place during the close encounter has been extensively discussed [11,12] in connection with experimental investigations of charge-transfer excitation of $n = 2$ states of hydrogen atoms by H^+-He collisions at moderate energies [13–15]. According to the molecular orbital (MO) model [11], one electron can be promoted to $n = 2$ united-atom states after an initial diabatic $1s\sigma$-$2p\sigma$ transition. During the final phase the collision system then evolves from the $n = 2$ united-atom states via the

TABLE I. Electric-field strength F_{ac} of the $1s5d$, $1s5f$, and $1s5g$ singlet-triplet anticrossings, the measured relative population numbers P_{exp} of the singlet Stark substates at the anticrossings for $F < 0$ and $F > 0$, and the squared moduli $|c(F_{ac})|^2$ of the expansion coefficients $c(F_{ac})$ (see text).

Crossing sublevels	F_{ac} in kV/cm	P_{exp} $F<0$	P_{exp} $F>0$	$\lvert c(F_{ac})\rvert^2$ $F<0$	$\lvert c(F_{ac})\rvert^2$ $F>0$
$1s5d$ $^1\Pi \times {}^3\Delta$	4.71	1.0	<0.1	0.86	0.06
$^1\Sigma \times {}^3\Pi$	5.74	1.6	0.1	0.49	0.04
				(0.41)	(0.00)
$^1\Pi \times {}^3\Pi$	7.82	0.9	<0.2	0.89	0.03
$^1\Pi \times {}^3\Sigma$	10.01	0.9	<0.1	0.91	0.02
$1s5f$ $^1\Pi \times {}^3\Sigma$	6.50	<0.1	0.3	0.00	0.08
$^1\Sigma \times {}^3\Pi$	6.60			0.02	0.05
				(0.25)	(0.00)
$^1\Pi \times {}^3\Pi$	7.06	<0.2	<0.2	0.00	0.07
$^1\Pi \times {}^3\Delta$	9.73	<0.2	<0.2	0.00	0.09
$1s5g$ $^1\Pi \times {}^3\Pi$	6.36	<0.2	0.6	0.00	0.56
$^1\Sigma \times {}^3\Pi$	8.90	<0.3	0.4	0.02	0.15
				(0.02)	(0.77)

molecular $2p\sigma$, $2p\pi$, or $2s\sigma$ states to the separated-atom states observed in the experiments. Since the transition from the molecular states to the separated-atom state is strongly nonadiabatic, not only $n=2$ separated-atom states but also $n>2$ states with $\Lambda \leq 1$ are populated. Recently, when analyzing H_2^+-He [5] and He-He collisions [6], we pointed out that the promotion to $n>2$ states is provoked by inertial forces.

Considering H^+-He collisions, the promotion of electrons during the final phase can be described more precisely. After the close encounter, the $n=2$ state electron is moving in an H_2^{++}-like two-center Coulomb potential of the proton and the He^+ core. This motion can be described by MO saddle dynamics introduced by Rost and Briggs [16]. According to the MO saddle dynamics of the H_2^+ system, an electron starting from the united-atom states $1s\sigma$, $2s\sigma$, and $2p\pi$ can be promoted during the final phase of the collision along the in-saddle sequences of MO potentials $1s\sigma$-$3d\sigma$-$5g\sigma\ldots$, $2s\sigma$-$4d\sigma$-$6g\sigma\ldots$, and $2p\pi$-$4f\pi$-$6h\pi\ldots$, respectively. The orbitals of a sequence are connected by avoided crossings at interatomic separations where the molecular state transforms to a separated-atom state. Each sequence gives rise to the excitation of exactly one parabolic Stark state $|n;n_1,n_2,m\rangle$ of each separated atom with given principal quantum number n. For $n=5$, one finds that the $1s\sigma$, $2s\sigma$, and $2p\pi$ sequences lead to the parabolic states $|5;0,4,0\rangle$, $|5;1,3,0\rangle$, and $|5;0,3,\pm 1\rangle$, respectively.

Assuming that these parabolic states are excited selectively by 12.5 keV proton impact, we calculated the expansion coefficients $c(F)=\langle 5;n_1,n_2,m|1s5l\,^1\Lambda;F\rangle$ and deduced the relative population numbers $|c(F)|^2$ of the singlet Stark substates at the anticrossings for $F<0$ and $F>0$ (Table 1). The relative population of the $^1\Sigma$ Stark states may arise from promotion along the $1s\sigma$ or the $2s\sigma$ sequence. Accordingly, we calculated the population numbers resulting from the impact-excited states $|5;0,4,0\rangle$ and $|5;1,3,0\rangle$ (Table I; the latter ones are in parentheses). The relative population of the $^1\Pi$ states was calculated by assuming that the impact-excited states are $|5;0,3,\pm 1\rangle$. The population numbers $|c(F)|^2$ are to be compared with the experimental values $P_{\rm exp}$. They were deduced from the relative amplitudes of the anticrossing signals taking into account the broadening of the signals due to the field inhomogeneity and calculated branching ratios for the decay of the Stark states. Regarding the $^1\Pi$ states, the calculated population numbers $|c(F)|^2$ agree reasonably well with the experimental values $P_{\rm exp}$. This agreement confirms that saddle dynamics, predicting a unique population distribution for the $^1\Pi$ states, are well suited for describing the final phase evolution. Excitation of the $^1\Sigma$ states, which may be reached via the $1s\sigma$ and $2s\sigma$ in-saddle sequences, proceeds mainly via the $1s\sigma$ sequence. In particular, the signals found at $F=+5.7$ and $+8.9$ kV/cm and the absence of a signal at -6.6 kV/cm show that the $2s\sigma$ sequence is less important. Overall agreement between the calculated and experimental populations numbers is obtained by assuming that the parabolic Stark states $|5;0,4,0\rangle$ and $|5;0,3,\pm 1\rangle$ are collisionally excited in the ratio 3:1. This interpretation of our experimental results clearly emphasizes that quasimolecular effects are essential for H^+-He collisions at proton velocities $v_p \approx 0.7$ a.u. It should be noted that for these collisions a molecular excitation mechanism had already been conjectured by van Eck, de Heer, and Kistemaker in 1964 [9], when discussing maxima of $1snd$ excitation cross sections in the energy region of 10–15 keV.

Some important conclusions can be drawn from these results regarding the basic mechanism responsible for excitation in H^+-He collisions. In particular, we conclude that during the close encounter excitation of an electron to the $3d\sigma$ state is more likely than to the $2s\sigma$ state. This finding sheds new light not only on the excitation of helium atoms but also on the charge-exchange excitation of the $n=2$ states of hydrogen by H^+-He collisions, and may dissolve discrepancies so far existing between theory and experiment. Polarization studies on the Ly-α line [15] indicated that the population of the $2p$ Zeeman substate with $m=0$ is significantly higher than expected theoretically [11]. However, the theoretical treatment was based on the assumption that only promotion via the $2p\sigma$ MO contributes to the excitation process. We conclude from our experimental results that the excitation of σ states proceeds more likely via an initial evolution along the $(1s\sigma)^2$ potential (which predominates by 2 orders of magnitude [11]). Only when the atoms separate is one electron promoted to the $3d\sigma$ orbital by a mechanism similar to $1s\sigma$-$3d\sigma$ transitions in the symmetric H_2^+ system as suggested by MO saddle dynamics.

This close-encounter process may then be followed by either an adiabatic transition to the parabolic Stark state $|2;0,1,0\rangle$ of the separated atoms which has an asymmetric charge distribution agreeing in sign with that observed experimentally [4], or by diabatic transitions along the $1s\sigma$ in-saddle sequence leading to higher excited states of hydrogen and helium. Though this mechanism seems to be predominantly responsible for the excitation of $m=0$ states by H^+-He collisions, it is certainly much less important in collisions of hydrogen atoms with helium. In this three-electron system, one electron is always initially promoted along the $2p\sigma$ orbital [17]. Therefore, population of the $2s\sigma$ orbital by radial coupling may be more likely than population of the $3d\sigma$ orbital by MO saddle dynamics. Indeed, that seems to be the case. The $2s\sigma$ orbital of H_2^+ is adiabatically connected to the $|2;1,0,0\rangle$ state. Therefore, it is not surprising that the measured electric dipole moments of $H(n=2)$ states excited by H+He collisions [3,4] are opposite to the electric dipole moments found for H^+-He collisions.

In summary, the electric-field anticrossing technique provides an excellent experimental tool for measuring electric dipole moments of impact-excited states of He I. These dipole moments are formed by inertial forces. MO saddle dynamics seem to be the appropriate basis for a basic understanding of the evolution of the impact-excited state during the final phase of the collision process, and allows us to identify the precursor molecular state of the collision system arising from the close encounter. The conclusions drawn here with respect to the H^+-He system may initiate new theoretical investigations of this fundamental collision system.

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[1] C. C. Havener, W. B. Westerveld, J. S. Risley, N. H. Tolk, and J. C. Tully, Phys. Rev. Lett. **48**, 926 (1982).

[2] J. R. Ashburn, R. A. Cline, P. J. M. van der Burgt, W. B. Westerveld, and J. S. Risely, Phys. Rev. A **41**, 2407 (1990).

[3] R. Krotkov and J. Stone, Phys. Rev. A **22**, 473 (1980).

[4] R. Hippler, O. Plotzke, W. Harbich, H. Madeheim, H. Kleinpoppen, and H. O. Lutz, Z. Phys. D **18**, 61 (1991).

[5] A. S. Aynacioglu, S. Heumann, and G. v. Oppen, Phys. Rev. Lett. **64**, 1879 (1990).

[6] M. Hanselmann, A. S. Aynacioglu, and G. v. Oppen, Phys. Lett. A **175**, 314 (1993).

[7] D. Kaiser, Y.-Q. Liu, and G. v. Oppen, J. Phys. B **26**, 363 (1993).

[8] A. S. Aynacioglu, G. v. Oppen, and R. Müller, Z. Phys. D **6**, 155 (1987).

[9] J. van Eck, F. J. De Heer, and J. Kistemaker, Physica (Utrecht) **30**, 1171 (1964).

[10] Y.-Q. Liu and G. v. Oppen, J. Phys. B **25**, L37 (1992).

[11] J. Macek and Ch. Wang, Phys. Rev. A **34**, 1787 (1986).

[12] S. A. Slim, E. L. Heck, B. H. Bransden, and D. R. Flower, J. Phys. B **24**, 1683 (1991).

[13] D. W. Mueller and D. H. Jaecks, Phys. Rev. A **32**, 2650 (1985).

[14] R. Hippler, W. Harbich, M. Faust, H. O. Lutz, and L. J. Dubé, J. Phys. B **19**, 1507 (1986).

[15] R. Hippler, M. Faust, R. Wolf, H. Kleinpoppen, and H. O. Lutz, Phys. Rev. A **36**, 4644 (1987).

[16] J. M. Rost and J. S. Briggs, J. Phys. B **24**, 4293 (1991).

[17] M. Kumura and N. F. Lane, Phys. Rev. A **37**, 2900 (1988).