

Strong Effects of Initial Orbital Alignment Observed for Electron Capture in keV H^+ -Na(3p) Collisions

D. Doweck, J. C. Houver, J. Pommier, C. Richter, and T. Royer

*Laboratoire des Collisions Atomiques et Moléculaires, Bâtiment 351, Université Paris-Sud,
F-91405 Orsay CEDEX, France*

N. Andersen and B. Palsdottir

Physics Laboratory, H. C. Orsted Institute, DK-2100 Copenhagen, Denmark

(Received 9 February 1990)

Electron capture in keV collisions of protons with sodium atoms in the excited Na(3p) state is studied. The initial orbital alignment of the valence electron is controlled by the polarization of the exciting light. Capture into H(n) levels is measured for light polarization parallel and perpendicular to the proton beam direction. For $n=2$ the capture cross section is about 35% larger for an orbital aligned parallel than for one perpendicular to the beam direction, at all energies. However, for $n \geq 3$ the alignment effect varies dramatically with energy, supporting recent theoretical results.

PACS numbers: 34.50.Rk, 34.50.Pi, 34.70.+e

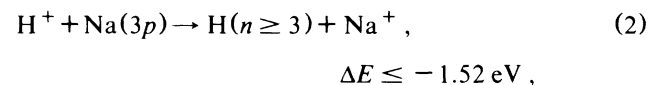
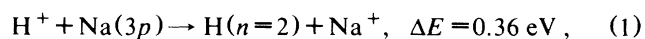
The study of alignment effects on the outcome of binary collision events has in recent years developed into a powerful tool for a deeper understanding of a wide variety of fundamental processes. The experimental technique common to all these studies has been the use of a laser to excite an atomic beam and control and vary the orbital alignment of the excited state through the direction of linear polarization of the laser light.

In this way Kircz, Morgenstern, and Nienhuis¹ observed a strong alignment effect on associative ionization of two Na(3p) atoms, revealing that the main reaction channel proceeds along a $^3\Sigma$ curve of the quasimolecule.² Rettner and Zare³ found a pronounced variation with initial Ca(1P_1) alignment in reactive collisions with HCl and Cl₂, again a fingerprint of strong molecular-orbital symmetry effects. The results motivated also speculations about the role of the orbital following and the concept of a locking or decoupling radius, inside which the electronic motion approximately follows the rotating internuclear axis, while staying space-fixed outside. These ideas turned out to be very powerful also for the interpretation of observed pronounced alignment dependences for such diverse processes as Ca(1P_1 - 3P_J) electronic energy transfer in thermal collisions with rare gases studied by Hale, Hertel, and Leone,⁴ collisional redistribution of light in Ba rare-gas collisions,⁵ resonant charge transfer in low-energy Na⁺-Na(3p) collisions analyzed by Hertel and co-workers,⁶ and intramultiplet mixing in the Na(3p)-He system.⁷ Reviews by Hertel and co-workers⁸ and Leone⁹ summarize the present situation.

However, for all the reactions listed above the collision velocity v_c is well below the velocity v_e of the active electron, motivating a quasimolecular interpretation. What happens in the region where $v_c \approx v_e$ is still an open question though many processes have their maximum cross section in this range. This paper reports the first study of effects of initial alignment at such velocities, to our

knowledge. The H⁺-Na(3p) quasi-one-electron system was chosen as a prototype for an investigation of non-resonant charge transfer. We have observed a strong polarization dependence of charge transfer in 0.5–2-keV H⁺-Na(3p) collisions [$v_c = v(3p)$ near 2-keV proton energy], varying with proton impact energy and principal quantum number n of the hydrogen atoms formed.

The H⁺-Na(3s) system has been the subject of many detailed studies, theoretically¹⁰ as well as experimentally.¹¹ However, results for charge transfer in H⁺-Na(3p) collisions have been obtained only recently.^{12,13} Here we analyze the alignment dependence of the two dominant inelastic channels:



where ΔE is the energy defect, with $\Delta E > 0$ (< 0) for an exothermic (endothermic) process.

The experimental setup has been described in detail earlier,¹² in an experiment that demonstrated a strong enhancement of the electron-capture probability from the Na(3p) state compared to Na(3s). Capture into the various H(n) levels are identified by time-of-flight (TOF) analysis of the scattered H atoms. Briefly, a well-collimated H⁺-ion beam of energy E is chopped and crosses at right angle a Na beam produced in a quasisupersonic expansion. The temperature of the oven is selected to yield a target density in the 10¹¹-atoms/cm³ range, thus avoiding radiation trapping.¹⁴ The effective fraction α of excited Na(3p) atoms is measured directly^{12,15} and is typically 10%. For the polarization-dependence measurements we inserted a Pockels cell in the laser path. A channel-plate detector is located at a distance $L = 4.50$ or 7.50 m from the collision volume,

with an angular acceptance of $\Delta\theta=0.5^\circ$ or 0.15° , respectively. When the detector is fixed at 4.50 m, the energy-loss spectra reflect the total cross sections.

Figure 1 displays hydrogen-atom energy-defect spectra for the $H^+-Na(3s \text{ or } 3p)$ collisions at $E=2$ keV and $L=7.50$ m. Figure 1(a) corresponds to the $H^+-Na(3s)$ collision for which the $H(n=2)+Na^+$ channel is dominant. Figures 1(b) and 1(c) correspond to the $H^+-Na(3p)$ collision and highlight the dominance of the reactions (1) and (2). With α defined as above, the spectra are obtained from the weighted differences $I_{on}^{\parallel} - (1-\alpha)I_{off}^{\parallel}$ and $I_{on}^{\perp} - (1-\alpha)I_{off}^{\perp}$, respectively, where I_{off}^{\parallel} , I_{on}^{\parallel} , and I_{on}^{\perp} are the intensities for spectra accumulat-

ed without and with lasers for light polarization directions parallel (\parallel) and perpendicular (\perp) to the proton beam.

Analysis of Figs. 1(b) and 1(c) shows that the $n=2$ peak area decreases by 10% when the laser polarization direction is rotated from being parallel to perpendicular to the collision velocity. This result is found at all energies investigated. The dependence is very different for the $n \geq 3$ peak: At 2 keV $H(n \geq 3)$ production is favored when the laser polarization is perpendicular to the collision velocity. However, at 1 keV this effect is reversed, so capture is favored here when the laser polarization is parallel to the collision velocity.

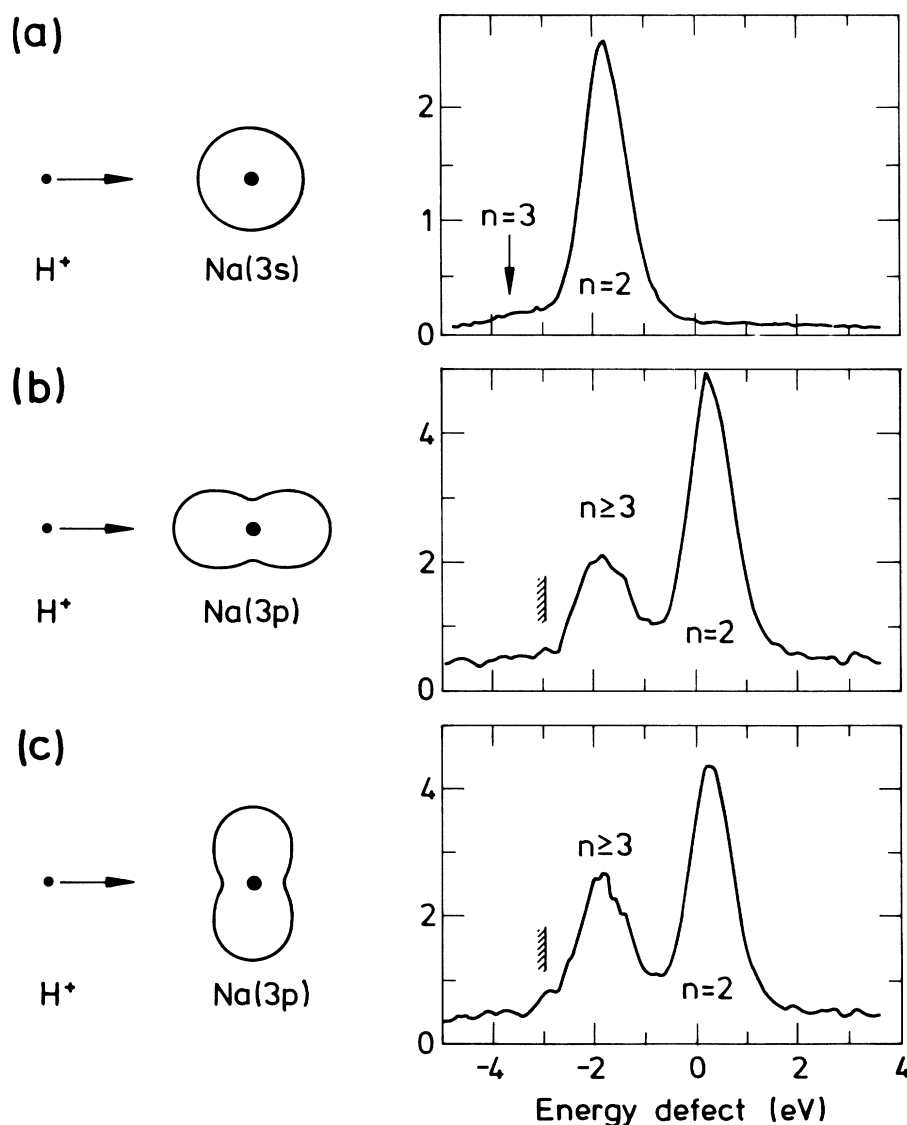


FIG. 1. Energy-defect spectra for forward-scattered neutral hydrogen atoms $H(n)$ produced by electron capture from sodium atoms (a) in the $Na(3s)$ ground state, and (b) in the $Na(3p)$ excited state prepared by laser light linearly polarized parallel and (c) perpendicular to the incident proton beam. The proton beam energy is 2 keV. The ordinate scales are in arbitrary but comparable units. The $Na(3p)$ charge clouds shown have rotational symmetry about their major axis.

In order to analyze the observed anisotropy in terms of atomic orbitals, one has to take into account that the two polarization directions (\parallel and \perp) do not correspond to preparation of *pure* $m_L=0$ p orbitals, which we label (\parallel) σ and (\perp) π consistent with the notation of molecular physics. The hyperfine structure causes a scrambling of the orbitals, the details of which depend on the specific hyperfine transition of the 3^2S-3^2P pumping scheme.¹⁴ When as here the $F=2-F=3$ transition is used, the two situations yield (\parallel) $\frac{5}{9}\sigma + \frac{4}{9}\pi$ and (\perp) $\frac{2}{9}\sigma + \frac{7}{9}\pi$. The left column of Fig. 1 shows the angular part of the resulting average sodium valence electron density (with the laser beam coming from a direction perpendicular to the plane of the figure). Thus, the difference in behavior of σ and π orbitals is significantly damped.

Using these coefficients, the dependence of the electron-capture probability on the initial alignment of the $\text{Na}(3p)$ orbital can now be discussed in terms of $\sigma_\Sigma(n)$ and $\sigma_\Pi(n)$ cross sections for each $\text{H}(n)$ channel populated in the $\text{H}^+-\text{Na}(3p)$ collision, where Σ and Π label the molecular symmetry of the entrance channel in the $R \rightarrow \infty$ asymptotic limit. The relative cross sections $\sigma_\Sigma:\sigma_\Pi$ are derived after integration of the peaks of the TOF spectra. We define the anisotropy parameter $A(n)$, $-1 \leq A \leq 1$, by

$$A(n) = [\sigma_\Sigma(n) - \sigma_\Pi(n)] / [\sigma_\Sigma(n) + \sigma_\Pi(n)]. \quad (3)$$

Figure 2 displays the variation of the anisotropy parameter $A(n)$, or the $\sigma_\Sigma(n):\sigma_\Pi(n)$ cross-section ratio, as a function of collision energy. The error bars are obtained after statistical analysis of the fluctuations in the various sets of measurements. Each data point represents typically an average of five measurements. The results underline the different behavior of capture into the $\text{H}(n=2)$ and $\text{H}(n \geq 3)$ levels. For electron capture to

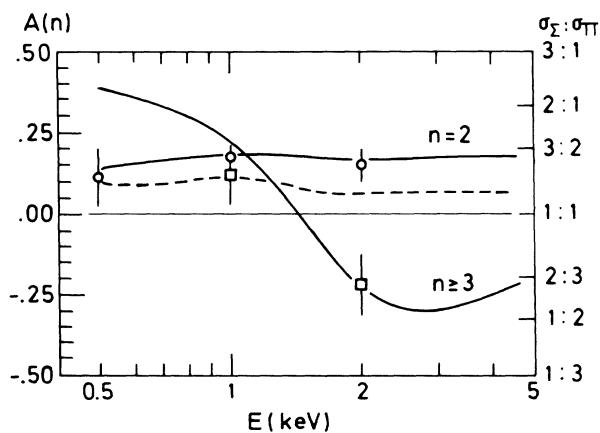


FIG. 2. The anisotropy parameter $A(n)$ defined in Eq. (3) and the cross-section ratio $\sigma_\Sigma(n):\sigma_\Pi(n)$ as a function of incident proton energy E . Present results are for $n=2$ (\circ) and $n \geq 3$ (\square). Theoretical curves: —, Ref. 16 ($n=2, n \geq 3$); ---, Ref. 17 ($n=2$).

the $\text{H}(n=2)$ level the σ_Σ cross section is about 35% larger than the σ_Π cross section at the three energies investigated. The size and weak energy dependence of $A(2)$ is strikingly similar to what was found by Hertel and co-workers⁶ for $\text{Na}^+-\text{Na}(3p)$ resonant charge exchange at much lower velocities. Their numbers correspond to $A(\text{Na}(3p)) \approx 0.25$ at $v_c = 0.013$ a.u. (compared to our velocities of 0.14–0.28 a.u.). However, the behavior of $A(3)$ is remarkably different: At 1 keV we still find that capture is favored for the Σ symmetry compared to the Π symmetry, but this situation is *reversed* at 2 keV ruling out a simple geometrical interpretation. Unfortunately, attempts at measuring $A(3)$ at 0.5 keV failed because the $n=3$ cross sections are vanishingly small here.

The results are compared with values extracted from calculations of Fritsch¹⁶ ($n=2,3$), who used a 49-state atomic basis, and recent calculations of Courbin *et al.*¹⁷ ($n=2$), using a 19-state molecular basis. The theoretical curves compare well with the experimental findings; in particular, the dramatic energy variation of $A(3)$ is reproduced.

Despite this agreement from the elaborate theoretical models no clear interpretation of these findings has yet emerged in terms of simple physical pictures. Thus, further scrutiny of dynamical calculations seems desirable, including, e.g., a study of the development of the alignment angle of the electron charge cloud along the trajectory,⁸ to see if the concept of a locking or decoupling radius is still a useful approximation at higher velocities, or whether new concepts can be developed that may be generalized to other systems and processes in this velocity range. Only when this goal has been achieved the understanding of alignment effects, i.e., the influence of the *shape* of the electron cloud, will have reached a stage for high-energy processes as satisfactory as in the low-energy quasimolecular regime.

Finally, we note that a corresponding development concerning the role of the sense of rotation of the active electron in its circular orbit, i.e., the aspects of its *dynamics*, remains a challenge for the future. We are accordingly pursuing investigations of right-left asymmetries of differential cross sections for atoms oriented by circularly polarized light, analogous to the beautiful low-energy results of Düren, Hasselbrink, and Tisher¹⁸ and Hertel and co-workers.⁶

We gratefully acknowledge W. Fritsch for communication of results prior to publication. Financial support by the Committee for the Development of European Science and Technology programme and Institut Français (Copenhagen) is gratefully acknowledged. Laboratoire de Collisions Atomiques et Moléculaires is Unité Associée au CNRS No. 281.

¹J. G. Kircz, R. Morgenstern, and G. Nienhuis, Phys. Rev. Lett. **48**, 610 (1982).

²F. Masnou-Seeuws, in Proceedings of the Sixteenth International Conference on the Physics of Electronic and Atomic Collisions, Book of Invited Papers, edited by A. Dalgarno (North-Holland, Amsterdam, to be published).

³C. T. Rettner and R. N. Zare, *J. Chem. Phys.* **77**, 2416 (1982).

⁴M. O. Hale, I. V. Hertel, and S. R. Leone, *Phys. Rev. Lett.* **53**, 2296 (1984).

⁵W. J. Alford, N. Andersen, K. Burnett, and J. Cooper, *Phys. Rev. A* **30**, 2366 (1984).

⁶A. Bähring, I. V. Hertel, E. Meyer, and H. Schmidt, *Phys. Rev. Lett.* **53**, 1433 (1984); R. Witte, E. E. B. Campbell, C. Richter, H. Schmidt, and I. V. Hertel, *Z. Phys. D* **5**, 101 (1987).

⁷M. P. I. Manders, J. P. J. Driessen, H. C. W. Beijerinck, and B. J. Verhaar, *Phys. Rev. Lett.* **57**, 1577 (1986).

⁸I. V. Hertel, H. Schmidt, A. Bähring, and E. Meyer, *Rep. Prog. Phys.* **48**, 375 (1985); E. E. B. Campbell, H. Schmidt, and I. V. Hertel, *Adv. Chem. Phys.* **72**, 37 (1988).

⁹S. R. Leone, in *Selectivity in Chemical Reactions*, edited by

J. C. Whitehead (Kluwer Academic, New York, 1988), p. 245.

¹⁰See R. Shingal and B. H. Bransden, *J. Phys. B* **20**, 4815 (1987), and references therein.

¹¹See F. Aumayr, G. Lakits, and H. Winter, *J. Phys. B* **20**, 2025 (1987), and references therein.

¹²T. Royer, D. Doweck, J. C. Houver, J. Pommier, and N. Andersen, *Z. Phys. D* **10**, 45 (1988), and references therein.

¹³R. J. Allan, R. Shingal, and D. R. Flower, *J. Phys. B* **19**, L251 (1986).

¹⁴A. Fisher and I. V. Hertel, *Z. Phys. A* **304**, 103 (1982).

¹⁵J. C. Houver, D. Doweck, J. Pommier, and C. Richter, *J. Phys. B* **22**, L585 (1989).

¹⁶W. Fritsch, *Phys. Rev. A* **30**, 1135 (1984); **35**, 2342 (1987); (private communication).

¹⁷C. Courbin, R. J. Allan, P. Salas, and P. Wahnon (to be published).

¹⁸R. Düren, E. Hasselbrink, and H. Tisher, *Phys. Rev. Lett.* **50**, 1983 (1983); R. Düren and E. Hasselbrink, *J. Chem. Phys.* **85**, 1880 (1986).