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Cross sections and coherence terms for associative ionization of two differently excited Na(3p) atoms

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The associative ionization process in thermal Na(3p)–Na(3p) encounters has been studied in a series of crossed-beam experiments where the light polarization of the two laser beams preparing the excited atoms before collision was varied independently. It is shown how in this way maximum possible information for our geometry is extracted about the dependence of the ion formation process on the shape and spatial orientation of the electron clouds of the two approaching atoms, including all coherence terms. The experimental findings are discussed in the light of recent theoretical results for the states of the Na₂ molecule. It is concluded that just a few of the possible geometrical approaches are favorable for molecular-ion formation.

I. INTRODUCTION

The progress in tunable laser technology has opened up new possibilities for studies of thermal atomic collision events in which one or both of the colliding species are in an excited state. Collisions of this kind may lead to a rich variety of processes, such as "energy pooling" and formation of molecules with varying degree of excitation, which apart from their intrinsic interest are of fundamental importance in fields such as plasma physics, astrophysics, atmospheric science, photochemistry, and related fields.

The collision between two Na atoms resonantly excited to the 3p state has been the favorite choice of study for many groups. At a first glance this might look as a most simple system. However, a long series of experimental^{1–16} and theoretical^{17–24} investigations have revealed surprisingly rich features, and we are still far from a satisfactory understanding of even the main findings. Figure 1 shows schematically a few of the molecular potential curves of the Na dimer and their dissociation limits. Notice that the combined excitation energy of two Na(3p) atoms is very close to the energy of some singly excited levels, such as Na(5s,4d,4f,5p). Therefore a likely outcome of an encounter is excitation transfer, i.e.,^{12–15}

an "energy pooling" process. A second possible exit channel would be ion pair formation Na⁺ + Na[−] which, however, for the kinetic energies available in our experiment is not accessible. One particularly interesting aspect of Fig. 1 is the alternative possibility of associative ionization

since the minimum of the Na₂⁺ ground state potential curve has an energy of 51 meV below the combined energy of the two excited atoms.^{25,26} Kircz *et al.*⁴ showed that the likeli-

hood of this process depends strongly on the polarization properties of the exciting laser light. This finding drew attention to the possibility of using the laser light to accurately control and manipulate the shape of the excited electron clouds as well as their orientation in space before the collision. In this way one can to some extent select which states to populate among the 12 molecular states originating from the Na(3p) + Na(3p) asymptote.^{18–21} Theoretical findings¹⁹ indicate that of these states only one or two are expected to cross into the Na₂⁺ continuum at an energy accessible in thermal collisions. This observation, and the strong dependence on laser light polarization, may suggest that just a few of the many possible geometrical approaches of the two excited atoms are efficient for molecular-ion production. Recent theoretical^{20,21} and experimental⁶ efforts are directed towards further exploring this possibility. Related associative ionization studies on K(4p) + K(4p) collisions, by Pauly and co-workers,²⁷ are in progress. Other studies have

FIG. 1. A schematic diagram of some potential curves and dissociation limits of importance for the outcome of a Na(3p)–Na(3p) collision. It is based partially on Refs. 15, 16, 19, 25, and 26. The arrows indicate the lower and upper limit for the center-of-mass energy in our experiment. The values correspond to collision velocities $v_c = 900$ and 2300 m/s.

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addressed the electron production^{2,3} and the rotational angular momentum of the molecular ion.^{8,9} One motivation for these experiments is their relevance to the astrophysically interesting problem of associative ionization and dissociative recombination in H–H⁺ encounters.²⁸

Interpretation of the results of experiments is, however, at present much complicated by the fact that they typically are performed by crossing an atomic beam and a laser beam and collecting all dimer ions produced in the interaction region, thus integrating over all impact parameters and orientations of the collision plane. Furthermore, in a collision, the fixed orientation in space of the electronic orbital is disturbed at short internuclear distances at which the electronic motion is partially or fully locked to the direction of the rotating internuclear axis. This observation has led to the introduction of the concept of a “locking or decoupling radius” that marks the transition region from space-fixed to molecular axis-fixed behavior.^{29–32}

Therefore it is of value to carefully consider possible experimental schemes to extract maximum information about the reaction, and the present paper reports aims towards this goal. The main new experimental development compared to previous studies is the possibility to vary *independently* the polarization of two laser pump beams, thereby controlling the shape of the excited electron charge cloud of the two colliding atoms independently too. A much stricter attention to the preparation and control of the laser beams and atomic beams is necessary here (revealing that seemingly contradictory earlier results in the literature may partly be caused by incomplete definition of the exciting beam). How this is done is described in Sec. II. Theoretically, we use as a starting point the general scheme for analysis developed by Nienhuis¹⁸ and explore in Sec. III how various combinations of linearly and/or circularly polarized light yield information about diagonal and off-diagonal elements of the detection matrix. In Secs. IV and V we explore for the first time the possibility of a complete measurement of all elements of the detection matrix in our experimental geometry and give the experimental results. Based on this, Sec. VI discusses possible consequences for shapes and symmetries of the valence electron cloud configurations most efficient for molecule formation. Finally, Sec. VII summarizes conclusions and comments briefly on future prospects. A short description of our approach has been presented in a recent letter.³³

FIG. 2. Schematic overview of the apparatus.

II. EXPERIMENT

The experimental setup is shown schematically in Fig. 2. It is basically the same as in Refs. 6, 33, and 34. A detailed description can be found in Ref. 35. Two counterrunning beams of Na atoms are intersected at nearly right angles (87°) by laser light from a cw dye laser (Spectra Physics 380D), tuned to the $F_l = 2 \rightarrow F_u = 3$ hyperfine component of the $\text{Na}(3s)^2S_{1/2} \rightarrow \text{Na}(3p)^2P_{3/2}$ transition. The laser beam is expanded and directed through a rectangular diaphragm, resulting in a spatially homogeneous laser spot with a height of 9 mm and a width of 5 mm. After it has traversed the Na beams the laser beam is reflected into its own path.

The angular divergence of the Na beams in the direction of the laser light is only 4 mrad. The rectangular laser spot defines the interaction region, where ions can be formed according to process (2). From the oven temperatures and the geometry the atomic densities in the interaction region are estimated to be 4×10^9 and $6 \times 10^9/\text{cm}^3$ for the two beams, respectively. All ions created in the interaction region are extracted by a weak electric field (100 V/cm) and are counted by a high current channeltron. The fluorescence light is monitored by five photodiodes at various angles, as is shown in Fig. 3. Thereby we are able to keep track of the atomic density and the atomic polarization. The magnetic field in the interaction region is less than 5 mG.³⁴

Since the laser intersects the two Na beams at 87°, we can select the velocity class of atoms that can be excited by varying the laser frequency. The laser frequency is selected and stabilized by means of a third Na beam in a separate vacuum chamber.³⁶ The laser is stabilized at frequencies ν_c ranging from 20 to 120 MHz higher than the resonance frequency ν_0 . With this method we are able to select any collision velocity between 900 and 2300 m/s with a typical width of 250 m/s (FWHM).

Moreover, the nonperpendicular intersection implies that atoms of beam 2 are only excited by the direct beam, whereas atoms of beam 1 are only excited by the reflected laser beam. This means that the polarization of the atoms in beam 1 can be made different from the polarization of those in beam 2, simply by changing the laser polarization of the

FIG. 3. The position of the five photodiodes measuring the fluorescence light, with respect to the coordinate frame, in which we describe our collision system.

reflected beam. To take full advantage of this possibility we use the following retardation plates.

(1) In the incident laser beam we use a rotatable $\lambda/2$ plate in combination with a polaroid to rotate the polarization vector. Also, a $\lambda/4$ plate can be installed, in order to prepare circularly polarized light.

(2) In order to change the polarization of the reflected beam we can place either a rotatable $\lambda/4$ plate or a rotatable $\lambda/8$ plate. Since the laser beam passes this retardation plate twice, the $\lambda/4$ plate acts as a $\lambda/2$ plate and the $\lambda/8$ plate as a $\lambda/4$ plate.

With the $\lambda/4$ plate and linearly polarized incident light we can rotate the polarization vector to any desired angle, whereas the combination of the $\lambda/4$ plate and incident circularly polarized light enables us to control the helicity.

Finally, with the $\lambda/8$ plate, we can change incident linearly polarized light, with its polarization vector at an arbitrary angle, into circularly polarized light.

All retardation plates are stepper motor driven, and are rotated by means of our Apple II computer, which also controls the beam shutters, checks the laser frequency and the laser intensity, and reads and checks the signals from the channeltron as well as from the photodiodes.

A. Atomic polarization

1. Linearly (π) polarized light

For sufficiently high laser intensity a stationary population of the magnetic sublevels of the $F = 3$ state is obtained. In a coordinate frame with the z axis parallel to the light polarization vector the excited atoms are described by a diagonal density matrix with elements in ratios of 20:10:1:0 for $M_F = 0, \pm 1, \pm 2$, and ± 3 , respectively.³¹ From this one can deduce a density matrix for the purely electronic part of the wave function by taking the trace over the nuclear spin components M_I . The elements of the resulting diagonal matrix in the so-called J picture ($\rho_{1/2}$ and $\rho_{3/2}$) have ratios of 5:1 for $M_J = \pm 1/2$ and $\pm 3/2$, respectively. (J is the electronic angular momentum.) This matrix can further be reduced if only the orbital angular momentum L is important. Taking the trace over electronic spin components M_S one obtains a diagonal matrix in the L picture with elements (ρ_{-1} , ρ_0 , and ρ_1) in a ratio of 2:5:2 for $M_L = -1, 0, 1$, respectively.

2. Circularly (σ) polarized light

In this case and for stationary state conditions σ^+ light only populates the $M_F = 3$ sublevel and consequently only the $M_J = 3/2$ or the $M_L = 1$ substate, respectively. When applying σ^- light the magnetic sublevel with the reversed sign is populated.

B. Determination of the relative density of excited atoms

In order to analyze the data we need to know the relative density of excited atoms. We do that by monitoring the fluorescence signals. In general, the fluorescence intensity distribution of an atom decaying from a magnetic sublevel

$|M| = 1$ to $M = 0$, hence $\Delta M = \pm 1$ has the shape

$$I_{f,1} = \eta n_{e,1} (1 + \cos^2 \xi), \quad (3)$$

whereas a decay with $\Delta M = 0$ leads to

$$I_{f,0} = 2\eta n_{e,0} \sin^2 \xi \quad (4)$$

with ξ the angle between detector and polarization direction, $n_{e,1}$ and $n_{e,0}$ the number of atoms (per second) decaying with $|\Delta M| = 1$ and 0, respectively, and η the factor containing the efficiency and aperture of the detector.

If we use the L picture in our case, there is only a $M_L = 0$ ground level. The excited atoms are characterized by a diagonal density matrix ρ , and we get

$$I_f = \eta n_e \frac{(\rho_1 + \rho_{-1})(1 + \cos^2 \xi) + 2\rho_0 \sin^2 \xi}{(\rho_{-1} + \rho_0 + \rho_1)} \quad (5)$$

with n_e the total number of excited atoms, and ρ_i the relative population of magnetic sublevel i of the excited level.

For our experiment we want to determine ηn_e as well as ρ_{-1} , ρ_0 , and ρ_1 . Therefore we have installed five photodiodes, detecting fluorescence light in different directions. Figure 3 shows the position of the photodiodes.

1. π polarization

Since in this case $\rho_{-1} = \rho_1$, we can write for detection with photodiode 1:

$$I_{f,1} = \eta_1 n_e \frac{4\rho_1}{\rho_0 + 2\rho_1} \left(1 + \frac{\rho_0 - \rho_1}{2\rho_1} \sin^2 \xi \right). \quad (6)$$

As will be discussed in Sec. II D, the anisotropy coefficient $B \equiv (\rho_0 - \rho_1)/2\rho_1$ is dependent on the laser frequency, and thus in our experiment on the selected collision velocity. This means that the density of excited atoms n_e is not proportional to the signal of a photodiode detecting light at some angle ξ . The solution of this problem is that one has to detect light at $\xi = 54.7^\circ$, the "magic" angle, at which $\sin^2 \xi = 2/3$. Then Eq. (6) turns into

$$I_{f,1,\xi=54.7^\circ} = \eta_1 n_e \cdot \frac{4}{3}. \quad (7)$$

In fact, we always measure $I_{f,1}$ as a function of ξ , and performed a least-squares fit to Eq. (6). This serves three purposes:

(1) In this way we get a more reliable value for $I_{f,1}$ at 54.7° , and thus for $\eta_1 n_e$.

(2) We get a value for B which means that we are able to measure the relative population of magnetic substates of the excited atoms, and compare it to the so-called stationary state distribution. We found that B varies from 0.57 at 900 m/s to 0.80 at 2300 m/s in a very reproducible way. This means that ρ_0/ρ_1 varied from 2.14 to 2.60, or in the J picture $\rho_{1/2}/\rho_{3/2}$ from 3.5 to 5.6. In order to take this change into account in our theoretical description we define

$$Q \equiv \frac{\rho_{3/2} + \rho_{1/2}}{\rho_{3/2} - \rho_{1/2}} = \frac{2\rho_1 + \rho_0}{2(\rho_1 - \rho_0)} = -\frac{3 + 2B}{4B}. \quad (8)$$

(3) The velocity dependence of B also contains information about the quality of the linearly polarized light (see Sec. II C).

2. σ polarization

In this case the interference with other hyperfine transitions, which causes the variation of B in the π -polarization case, plays a minor role.³⁷ So, if we assume stationary state conditions to be fulfilled, we can write

$$I_f = \eta n_e (1 + \cos^2 \xi) \quad (9)$$

with ξ now the angle between the direction of propagation of the laser light and the fluorescence detector. Unfortunately, we are now unable to vary the angle ξ in order to fit I_f to Eq. (9) and check the stationary state conditions. Instead, we use three of our photodiodes. Photodiode 1 is at an angle $\xi = 90^\circ$, so

$$I_{f1} = \eta_1 n_e \quad (10)$$

which is directly comparable to Eq. (7).

Photodiodes 2 and 3 are at 54.7° and -54.7° , respectively, so their signals are

$$I_{f2,3} = \frac{4}{3} \eta_{2,3} n_e \quad (11)$$

To compare these signals to Eqs. (7) and (10), we need to know η_1/η_2 and η_1/η_3 . We can extract these ratios when we use linearly polarized light with the polarization vector parallel to the beam axis. Then the angle ξ is 90° for all three photodiodes and the ratios of the detected light signals directly give us η_1/η_2 and η_1/η_3 .

When measuring with circularly polarized light, we always checked agreement between Eqs. (10) and (11). It appeared that there was a systematic deviation of about 3%. This deviation did not show any collision velocity (frequency) dependence, so it may well be caused by a systematic error caused by a small displacement of any of the three photodiodes. Should it, in the worst case, really be caused by a deviation from stationary state conditions, it would mean that only about 3% of the excited atoms is in the $M_L = 0$ substate.

C. Polarization quality

One crucial experimental condition is the polarization quality of the laser light, expressed in the degree of linear polarization $P_L = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, and the degree of circular polarization $P_C = |I_- - I_+|/(I_- + I_+)$. The polarization quality of the direct laser beam could be measured easily, and both P_L and P_C exceeded 99.9% for linearly and circularly polarized light, respectively. Passing through the two vacuum windows did not influence this quality, as we checked experimentally.

The polarization quality of the reflected beam could not be measured directly. However, we could check this polarization in an indirect way by measuring the fluorescence distribution of the atoms excited by the reflected beam. In case the reflected beam was circularly polarized we could compare the three different signals (10) and (11). This is a good check, since the comparison is very sensitive to the population of the $M_L = 0$ sublevel. We never detected a deviation larger than the experimental error of 3%.

In the case of linearly polarized light we could use the value of B as a check. As shown in Sec. II B, B is sensitive to

the ratio ρ_0/ρ_1 , which would change if there were an important admixture of circularly polarized light. However, this ratio also changes as a function of collision velocity. Therefore we must always compare the B 's from atoms excited with the linearly polarized reflected laser beam to those excited with the direct laser beam.

In general, the B measured in the two atomic beams appeared to reproduce very well, except in one experiment, which for that reason had to be discarded. In Fig. 4 we show the comparison between a "regular" B and the one for which the degree of linear polarization was bad. The difference in B is about 0.1, which means that, e.g., at 1800 m/s the ratios $\rho_{-1}:\rho_0:\rho_1 = 2.5:2.4$ instead of 2.5:2, if we suppose the deviation is caused by an admixture of circularly polarized light.

D. Trapping

As already explained in our previous paper⁶ the variation of B as a function of collision velocity is caused by the influence of the nearby $F_l = 2 \rightarrow F_u = 2$ hyperfine transition, 59 MHz away.³⁸ A quantitative theoretical treatment of this effect would necessitate the use of optical Bloch equations, and lies beyond the scope of this paper. Qualitatively, the frequency dependence of the fluorescence anisotropy can be understood as follows. At small laser detunings many atoms "see" the laser light with a frequency lower than the resonance frequency ν_0 . In the extreme situation, the frequency becomes resonant to the $F_l = 2 \rightarrow F_u = 2$ transition, and the fluorescence of this transition is isotropic, i.e., $B = 0$.

On the other hand, at high detunings many atoms see the laser light with a frequency higher than ν_0 . In the extreme situation the frequency difference between the $F_u = 2$ and $F_u = 3$ levels becomes negligible: we look in the " J picture," and B becomes 1.5.

FIG. 4. Measurements of the anisotropy factor B of the emitted fluorescence light as a function of collision velocity, when exciting with linearly polarized (π) light. ● A representative example of the measurement of B on atoms excited by the direct laser beam. ○ A measurement on atoms excited by the reflected laser beam. The dotted line indicates the stationary state value (0.75). Comparison of ● and ○ shows that the anisotropy in case ○ is significantly lower, which is caused by a bad polarization quality of the reflected laser light. The experiment connected with ○ had to be discarded for that reason.

Of course, in our experimental situation we reach neither of these two extreme situations, but the tendency is clear: B changes from 0.57 to 0.80 as a function of laser frequency, its stationary state value being 0.75. As explained before, we are able to measure this B , and correct our equations for deviations from the stationary state value.

Apart from this "detuning" effect, we also get a certain fraction of the atoms excited into the $F_u = 2$ level itself. This level can act as a "trap," since 50% of the atoms decaying from this level end up in $F_l = 1$, from which they cannot be

FIG. 5. Illustration of how the velocity-selective excitation of Na takes place. The laser beam, intersecting with the Na beams at 87° , is stabilized on a frequency $\nu_0 + \nu_c$. In (A), $\nu_c = 80$ MHz. Then the direct laser beam excites atoms from atomic beam 2 (the left Maxwell-Boltzmann velocity distribution) with velocities around 900 m/s from $F_l = 2$ into the $F_u = 3$ level. The reflected laser beam does the same with Na-beam 1. The shaded area indicates the velocity class of atoms that can take part in the excitation process. (Of course the percentage of atoms actually excited is not 100 in the peak.) At higher velocities, however, atoms can be excited into the $F_u = 2$ level. In (A), that amount of excitable atoms is still extremely small, but as ν_c decreases [in (B), $\nu_c = 60$ MHz and in (C), 40 MHz] this amount increases. Furthermore, below $\nu_c = 60$ MHz the amount of atoms resonant with the $F_l = 2 \rightarrow F_u = 3$ transition decreases, so the density ratio $F_u = 2/F_u = 3$ increases. However, the shaded area gives an exaggerated impression of this ratio, since at the laser irradiance we use the $F_l = 2 \rightarrow F_u = 3$ transition is ≈ 50 times as effective as the $F_l = 2 \rightarrow F_u = 2$ transition. Still, in the case ν_c comes below 35 MHz [as in (D), where $\nu_c = 25$ MHz] the trapping effect connected with the $F_l = 2 \rightarrow F_u = 2$ transition becomes so important, that we cannot perform reliable cross section measurements anymore.

excited anymore. This fraction will be velocity dependent too, as clarified in Fig. 5. At high laser frequencies, there are no atoms in resonance with the $F_l = 2 \rightarrow F_u = 2$ transition but as the frequency gets lower, the number of atoms in the $F_u = 2$ level will increase, and this number will become considerable at detuning frequencies below 30 MHz.

Although this effect does not influence the velocity distribution of the $F_u = 3$ atoms, there are two good reasons to keep the ratio $F_u = 2/F_u = 3$ as small as possible. The average collision velocity will be larger than the results of calculations only dealing with $F_u = 3$, and the number of excited atoms will no longer be constant in any region of the spot. Especially, in our counterpropagating beam experiment this may introduce a spurious velocity dependence of the cross section, since especially at low collision velocities, where the ratio $F_u = 2/F_u = 3$ increases and the atoms have a longer passage time, this trapping effect simulates too low a cross section. To be sure that these effects do not influence our results by more than a few percent, we measure fluorescence intensities as a function of laser irradiance, to obtain so-called saturation curves. Apart from the measurement with the laser intersecting at right angles, from which we concluded that laser irradiances are to be kept smaller than 15 mW/cm^2 ,⁶ we now also measure saturation curves, for three detuning frequencies in the situation of the experiment, with the laser intersection at 87° . Results of these curves, and also a very accurate remeasuring of our curve at right angles, are shown in Fig. 6. In Fig. 6(A) are also shown the theoretical predictions, based on a numerical solution of rate equations. There is perfect agreement, apart of course for the higher part of the "linear" curves, where trapping becomes important. We used this deviation between theoretical and experimental curves for a simple model describing the trapping effect.³⁵ Detailed calculations including the trapping effect based on Bloch equations have been performed by Smith and co-workers.³⁹ Neither these, nor our calculations can be used directly for comparison with the 87° data. However, mutual comparison between the three experiments at different detuning frequencies shows that, although the trapping effect at 40 MHz starts at lower irradiances than in the other two cases, 8 mW/cm^2 (the value we used) is still in the "safe" region. When the detuning frequency goes still further down, this ceases being so (cf. Fig. 5). Therefore the lowest detuning frequency we used in these experiments was 35 MHz, limiting ourselves at the low side of the collision velocity scale to about 950 m/s.

III. THEORY

The process of associative ionization can be characterized by the ionization amplitudes $f(\alpha, \mathbf{v}_f \leftarrow M_A M_B, \mathbf{v}_c)$ which in the first place depend on the magnetic quantum numbers M_A and M_B of the colliding atoms, but also on the relative collision velocity $\mathbf{v}_c$, the velocity of the ejected electron $\mathbf{v}_f$, and the final state α of the molecular ion. Absolute square values of these amplitudes represent cross sections $\sigma(M_A, M_B) = |F(M_A M_B)|^2$, and the observed ion production rate can be written as

FIG. 6. (I) Experimental and theoretical saturation curves with the laser intersecting the Na beam at right angles. Experimental points: ($\square$) excitation with π light, fluorescence detected at $\theta = 90^\circ$, ($\triangle$) excitation with π light, detection at $\theta = 0^\circ$, ($\circ$) excitation with σ light, detection at $\theta = 90^\circ$. The curves are the result of our numerical calculations. There is very good agreement between theory and experiment, except for both π cases at higher irradiances, where trapping gets important. (II) Three measurements of saturation curves in our experimental situation, i.e., with the laser intersecting the Na beams at 87° . (A) The stabilization frequency of the laser $\nu_c = 40$ MHz, thereby selecting a collision velocity $v_c = 1050$ m/s. (B) $\nu_c = 70$ MHz, and $v_c = 1600$ m/s. (C) $\nu_c = 100$ MHz and $v_c = 2150$ m/s.

$$R = \int d\Omega_f \sum_{\alpha} \sum_{M_A M'_A} \sum_{M_B M'_B} f(M_A M_B) f^*(M'_A M'_B) \times \left(\frac{m_e v_f}{\mu} \right) \langle M_A | \rho | M'_A \rangle \langle M_B | \rho | M'_B \rangle. \quad (12)$$

Here $\langle M | \rho | M' \rangle$ represent elements of the density matrix ρ of the excited atoms (ρ_A and ρ_B for collision partners A and B , respectively). The integration is over all final velocities of the ejected electron. The summation is over the final quan-

tum numbers α of the molecular ion, and over all combinations $(M_A M'_A)$ and $(M_B M'_B)$. Furthermore, m_e is the electron mass and v_f its velocity, and μ is the reduced mass of the two initial collision partners.

Regarding the choice of the coordinate frame for the description of the process, an obvious possibility would be to choose the light direction as an axis of quantization, since this gives the simplest mathematics. However, if the coordinate frame has its z axis along the relative velocity of the

TABLE I. The expansion coefficients c_k in the L and the J picture, for stationary state conditions.

Polarization	c_0	c_1	c_2	c_3	
linear(π)	1/3	0	-2/3/6	0	L-picture
circular (σ^+)	1/3	1/2	1/6	0	
(σ^-)	1/3	-1/2	1/6	0	
linear (π)	1/2	0	-1/3	0	J-picture
circular (σ^+)	1/2	3/2/5	1/2	1/2/5	
(σ^-)	1/2	-3/2/5	1/2	-1/2/5	

collision partners, the experimental results can more easily be compared with theoretical potential curves which refer to the internuclear axis. This causes some complications, since the density matrices describing the excited atoms take their simplest form in a coordinate frame with z in the direction of the polarization vector when exciting with linearly polarized (π) light, or with z in the direction of the propagation of the laser beam when exciting with circularly polarized (σ) light. Therefore, we expand the density matrices of the excited atoms in terms of spherical tensors. This yields (for details see, e.g., Nienhuis¹⁷)

$$\rho = \sum_{k=0}^{2J} \sum_{q=0}^k c_k D_{q0}^{k*}(\alpha\beta\gamma) T_{kq}^\dagger. \quad (13)$$

Here the c_k are expansion coefficients, $D_{q0}^{k*}(\alpha\beta\gamma)$ are rotation matrices⁴⁰ inducing the rotation from the light frame to the collision frame [$q' = 0$ in Eq. (13) reflects the fact that the density matrix in the light frame is diagonal], and T_{kq} are irreducible spherical tensors. The c_k depend on the excitation mode (linearly or circularly polarized light) and also on the description of the excited atoms, which can be done either in an L picture, which takes only orbital angular momenta into account and thus neglects spin effects, or in a J picture, in which the total electronic angular momenta are taken into account. Furthermore, for nonstationary state conditions, they have to be corrected by using Q [see Eq. (8)]. Values of the c_k for the various cases (assuming stationary state) are given in Table I.

Also the detection operator G has to be expanded in terms of spherical tensors. Here G is defined by its matrix elements

$$\langle M_A' M_B' | G | M_A M_B \rangle = \int d\Omega_f \sum_{\alpha} f(M_A M_B) \times f^*(M_A' M_B') \left(\frac{m_e v_f}{\mu} \right). \quad (14)$$

This expansion yields

$$\begin{aligned} \bar{\sigma}_{11} &= \frac{1}{2}(\sigma_{11} + \sigma_{1-1}) = \frac{1}{6}(2p_L + 2\sqrt{2}s_L + t_L), \\ L \text{ picture: } \sigma_{10} &= \frac{1}{6}(2p_L - \sqrt{2}s_L - 2t_L), \\ \sigma_{00} &= \frac{1}{6}(2p_L - 4\sqrt{2}s_L + 4t_L); \end{aligned} \quad (17)$$

TABLE II. The expansion coefficients of the detection matrix G with their short names, their type and whether or not they appear in the L or J picture description.

Element	short	type	L/J-picture
$g(00;00)$	p	Diagonal	L/J
$g(10;10)$	q	Diagonal	L/J
$g(20;00)$	s	Diagonal	L/J
$g(20;20)$	t	Diagonal	L/J
$g(30;10)$	w	Diagonal	J
$g(30;30)$	y	Diagonal	J
$g(11;1-1)$	r	Off-diagonal	L/J
$g(21;1-1)$	i λ	Off-diagonal	L/J
$g(21;2-1)$	u	Off-diagonal	L/J
$g(22;2-2)$	v	Off-diagonal	L/J
$g(31;1-1)$	x	Off-diagonal	J
$g(31;2-1)$	i μ	Off-diagonal	J
$g(31;3-1)$	z	Off-diagonal	J
$g(32;2-2)$	i ν	Off-diagonal	J
$g(32;3-2)$	a	Off-diagonal	J
$g(33;3-3)$	b	Off-diagonal	J

$$G = \sum_{kqk'q'} g(kq;k'q') T_{kq} T_{k'q'}^\dagger. \quad (15)$$

Those coefficients g for which $q = q'$ can be expressed in terms of cross sections $\sigma(M, M')$, whereas the other ones represent the off-diagonal or coherence terms, connected to products of ionization amplitudes $f(M_A M_B) \cdot f^*(M_A' M_B')$ for which $M_A \neq M_A'$ or $M_B \neq M_B'$. However, it should be stated that there is no principle difference between the diagonal and off-diagonal elements and that they can be transferred into each other by selection of another coordinate frame. The ionization signal is then given by¹⁷

$$R = \sum_{kqk'q'} g(kq;k'q') c_k c_{k'} D_{q0}^{k*}(\alpha\beta\gamma) D_{q'0}^{k'}(\alpha'\beta'\gamma'), \quad (16)$$

where the dashed quantities now indicate their connection with the "other" collision partner. Nienhuis¹⁷ has shown how various symmetry relations can be exploited to reduce the number of independent coefficients $g(kq;k'q')$ that have to be taken into account. In order to simplify the equations we follow his notation and abbreviate the g coefficients by one letter. In Table II the abbreviations are given, together with their connection to diagonal or off-diagonal elements of the detection matrix G , thus having a cross section or a coherence character, respectively. Furthermore, Table II indicates whether or not they appear in the L - or J -picture description.

When the g coefficients are determined from experiment the related cross sections can simply be derived by the following equations:

$$J \text{ picture: } \begin{aligned} \bar{\sigma}_{3/2 \ 1/2} &= \frac{1}{2}(\sigma_{3/2 \ 1/2} + \sigma_{3/2-1/2}) = \frac{1}{4}(p_J - t_J), \\ \bar{\sigma}_{1/2 \ 1/2} &= \frac{1}{2}(\sigma_{1/2 \ 1/2} + \sigma_{1/2-1/2}) = \frac{1}{4}(p_J - 2s_J + t_J). \end{aligned} \quad (18)$$

We will now discuss which measurements must be performed to obtain the various g coefficients.

A. Both atoms excited with linearly (π) polarized light

With the linear polarization vector of the laser light forming an angle θ with the direction of Na-beam 1 (defined as z direction) the Euler angles of the rotation matrices $D_{q0}^k(\alpha\beta\gamma)$ reduce to $(\alpha\beta\gamma) = (0^\circ, \theta, 0^\circ)$ and are therefore given by $d_{q0}^k(\theta)$.⁴⁰ In this case an explicit expression for R is given by

$$R = p \cdot (c_0^\pi)^2 + \frac{1}{2} s c_0^\pi c_2^\pi [(3 \cos^2 \theta - 1) + (3 \cos^2 \theta' - 1)] + (c_2^\pi)^2 [\frac{1}{4} t (3 \cos^2 \theta - 1) (3 \cos^2 \theta' - 1) - 3u \sin \theta \cos \theta \sin \theta' \cos \theta' + \frac{3}{4} v \sin^2 \theta \sin^2 \theta'], \quad (19)$$

where the superscript π indicates the linear laser polarization.

For the specific choices we make for θ and θ' , the ionization signal can generally be written as¹⁷

$$R = R_0 + R_1 \cos 2\theta + R_2 \cos 4\theta. \quad (20)$$

1. Cases $\theta, \theta' = \theta$ and $\theta, \theta' = -\theta$

For these cases Eq. (19) indicates that direct information on the coherence term $u = g(2 \ 1; 2 \ -1)$ can be obtained from a set of two experiments in which $\theta = \theta'$ and $\theta = -\theta'$, respectively. The sum $R^{(\theta, \theta)} + R^{(\theta, -\theta)}$ of the corresponding ionization signals will not contain u , since the u term contributes with opposite signs to the signals, whereas the difference signal $R^{(\theta, \theta)} - R^{(\theta, -\theta)}$ will directly yield the quantity u .

For completeness we give the expressions for the Fourier coefficients in terms of the g coefficients:

$$\begin{aligned} R_0^{(\theta, \pm \theta)} &= p(c_0^\pi)^2 + \frac{1}{2} s(c_0^\pi c_2^\pi) + \frac{1}{32} (c_2^\pi)^2 (11t \mp 12u + 9v), \\ R_1^{(\theta, \pm \theta)} &= \frac{3}{2} s(c_0^\pi c_2^\pi) + \frac{3}{8} (c_2^\pi)^2 (t - v), \\ R_2^{(\theta, \pm \theta)} &= \frac{1}{32} (c_2^\pi)^2 (9t \pm 12u + 3v). \end{aligned} \quad (21)$$

2. Cases $\theta, \theta' = 0^\circ, 90^\circ$

Another useful set of measurements can be performed by keeping the angle θ' for excitation of one of the collision partners constant at $\theta' = 0^\circ$ or $\theta' = 90^\circ$. Evaluation of Eq. (19) and transformation to the general form (20) then yields for the case $\theta' = 0^\circ$ the Fourier coefficients

$$\begin{aligned} R_0^{(\theta, 0^\circ)} &= p(c_0^\pi)^2 + \frac{1}{4} s c_0^\pi c_2^\pi + \frac{1}{4} t (c_2^\pi)^2, \\ R_1^{(\theta, 0^\circ)} &= \frac{3}{4} s c_0^\pi c_2^\pi + \frac{3}{4} t (c_2^\pi)^2, \\ R_2^{(\theta, 0^\circ)} &= 0, \end{aligned} \quad (22)$$

and for the case $\theta' = 90^\circ$,

$$\begin{aligned} R_0^{(\theta, 90^\circ)} &= p(c_0^\pi)^2 - \frac{1}{4} s c_0^\pi c_2^\pi - \frac{1}{8} (c_2^\pi)^2 (t - 3v), \\ R_1^{(\theta, 90^\circ)} &= \frac{3}{4} s c_0^\pi c_2^\pi - \frac{3}{8} (c_2^\pi)^2 (t + v), \\ R_2^{(\theta, 90^\circ)} &= 0. \end{aligned} \quad (23)$$

As we have seen before, the coherence term u can directly be determined.³³ Unfortunately the sets of Eqs. (21)–(23) are not linearly independent and thus it is not possible to extract the cross section terms p , s , t and the coherence term v from the measurements corresponding to Eqs. (21)–(23). Therefore it is important to have additional possibilities for measurements, such as those described below.

It should be pointed out that various consistency checks on the experimental conditions are possible in view of the relations (21)–(23). It can, e.g., be verified, whether the signals $R^{(\theta, 0^\circ)}$ and $R^{(\theta, 90^\circ)}$ do indeed not show a $\cos 4\theta$ dependence [see Eqs. (22) and (23)]. Also the following relations between the various signals should be fulfilled:

$$\begin{aligned} R_1^{(\theta, +\theta)} &= R_1^{(\theta, -\theta)}, \\ R^{(\theta, 90^\circ)}(\theta = 0^\circ) &= R^{(\theta, 0^\circ)}(\theta = 90^\circ), \\ R^{(\theta, 90^\circ)}(\theta = 90^\circ) &= R^{(\theta, \theta)}(\theta = 90^\circ) = R^{(\theta, -\theta)}(\theta = 90^\circ), \\ R^{(\theta, 0^\circ)}(\theta = 0^\circ) &= R^{(\theta, \theta)}(\theta = 0^\circ) = R^{(\theta, -\theta)}(\theta = 0^\circ). \end{aligned} \quad (24)$$

Relations (24) imply that from the ten coefficients R [two times three from Eq. (21), two from Eq. (22), and two from Eq. (23)] only a maximum of four independent parameters can be determined.

B. Both atoms excited with circularly (σ) polarized light

In a coordinate frame with z pointing into the direction of the laser light, y along Na-beam 1 and 2 upwards the excited atoms are described by a diagonal density matrix. Rotation by the Euler angles $(\alpha\beta\gamma) = (-90^\circ, 90^\circ, 90^\circ)$ will transform the density matrix into the collision system with z along Na-beam 1.

Evaluating Eq. (16) we arrive—after some algebra—at the results for the signals R^{++} and R^{+-} corresponding to excitation of both atoms with parallel ($++$) or with anti-parallel ($+-$) angular momenta, respectively. It is interesting to see that the sum of these two signals

$$R^{++} + R^{+-} = 2(c_0^\sigma)^2 p - 2c_0^\sigma c_2^\sigma s + \frac{1}{2}(c_2^\sigma)^2 t + \frac{3}{2}(c_2^\sigma)^2 v \quad (25)$$

again only contains the cross section related terms p, s, t , and the coherence term v , which all occurred in the linear polarization case, whereas the difference signal

$$\begin{aligned} R^{+-} - R^{++} = & \frac{3}{8}c_3^{\sigma+}(c_3^{\sigma+} - c_3^{\sigma-})o' + \frac{3}{8}c_3^{\sigma+}(c_3^{\sigma+} - c_3^{\sigma-})z \\ & + c_1^{\sigma+}(c_1^{\sigma+} - c_1^{\sigma-})r \\ & - \frac{1}{4}\sqrt{6}[c_1^{\sigma+}(c_3^{\sigma+} - c_3^{\sigma-}) \\ & + c_3^{\sigma+}(c_1^{\sigma+} - c_1^{\sigma-})]x \end{aligned} \quad (26)$$

contains the coherence terms o', z, r , and x . This allows a check, in a very simple way, of how far these coherence terms influence the ionization signal. The number of independent coefficients, is by these measurements, increased by two to a total number of six.

C. Combination of linearly (π) and circularly (σ) polarized light

If one atom is excited by linearly polarized light (with the polarization vector again at variable angle with respect to the Na beams), and the other by circularly polarized light, the corresponding diagonal density matrices have to be transformed by rotation matrices $d(\theta)$ and $D(-90^\circ, 90^\circ, 90^\circ)$, respectively. Evaluating Eq. (16) we arrive at the following result:

$$\begin{aligned} R^{(\theta,+)} = & c_0^\pi c_0^\sigma p + \frac{1}{4}(c_2^\pi c_0^\sigma - 2c_0^\pi c_2^\sigma)s - \frac{1}{8}c_2^\pi c_2^\sigma t - \frac{3}{8}c_2^\pi c_2^\sigma v \\ & + \{\frac{3}{4}c_2^\pi c_2^\sigma s - \frac{3}{8}c_2^\pi c_2^\sigma t + \frac{3}{8}c_2^\pi c_2^\sigma v\} \cos 2\theta \\ & + \{\frac{1}{2}\sqrt{3}c_2^\pi c_1^{\sigma+}\lambda + \frac{1}{8}\sqrt{2}c_2^\pi c_3^{\sigma+}\mu\} \sin 2\theta \\ = & R_0^{(\theta,+)} + R_1^{(\theta,+)} \cos 2\theta + R_3^{(\theta,+)} \sin 2\theta. \end{aligned} \quad (27)$$

Notice that in this case the signal does not have the general θ dependence given by Eq. (20) but that in place of a $\cos 4\theta$ term now a $\sin 2\theta$ term shows up, which means that the ionization signal is no longer symmetric with respect to $\theta = 0^\circ$. The $\sin 2\theta$ dependence yields one more new parameter: $R_3^{(\theta,+)}$, a linear combination of λ and μ . The other two coefficients $R_0^{(\theta,+)}$ and $R_1^{(\theta,+)}$ are linear combinations of the previous coefficients. This means that a maximum of seven independent parameters can be determined by means of linearly and circularly polarized light propagating perpendicularly to the atomic beams. More parameters could be determined by using, e.g., a collinear geometry¹¹ or exploiting magnetic field effects.³⁴

TABLE III. Summary of the various detection schemes discussed in this section. Also the θ dependence is indicated.

case	Atom 1	Atom 2	θ -dependent terms $\cos 2\theta$ $\cos 4\theta$ $\sin 2\theta$		
$R(\theta, \theta)$			+	+	-
$R(\theta, -\theta)$			+	+	-
$R(\theta, 0^\circ)$			+	-	-
$R(\theta, 90^\circ)$			+	-	-
R^{++}			-	-	-
R^{+-}			-	-	-
$R(\theta, +)$			+	-	+

Table III summarizes the possibilities of the schemes discussed in this section.

IV. MEASUREMENTS AND RESULTS

A. Measurements

In Fig. 7 we show two examples of measurements in which both colliding atoms are excited with linearly polarized light, forming angles (θ, θ') with the atomic beams. In one case $\theta' = \theta$ is chosen and the other $\theta' = -\theta$. Also the fits to Eq. (20) are shown. As explained in Sec. III, the difference between the two sets of curves is proportional to the coherence contribution u . Clearly u is velocity dependent. Notice also that the measuring points for which $\theta' = \theta$ are equal to those for which $\theta' = -\theta$ within the error bars at $\theta = 0^\circ$, $\theta = 90^\circ$, and $\theta = 180^\circ$, as they should.

In Fig. 8 we show the cases in which θ' was kept on 0° or 90° , whereas θ was varied. Note that in the case of $\theta' = 0^\circ$ there is a strong polarization dependence, whereas in the other case polarization dependence is almost absent. Again, also the fits to Eq. (20) are shown, with $R_2 = 0$.

In this set of measurements, the ion signal at $\theta = 90^\circ$, $\theta = 0^\circ$ deviated from the signal at $\theta = 0^\circ$, $\theta' = 90^\circ$ by 5%–10%, an effect caused by a small θ' -dependent displacement of the reflected beam. Therefore we decided to renormalize the $\theta, \theta' = 90^\circ$ curve to the $\theta, \theta' = 0^\circ$ curve, thereby making one R coefficient a linear combination of the other three. For this we used one of the relations (24), so we did not lose an independent coefficient.

The case in which one atom is excited with left-hand circularly polarized light (σ^+) and the other one either with σ^+ or σ^- light of course only yields two experimental points

FIG. 7. Polarization dependence measurements for the cases $(\theta, \pm\theta)$ at two different collision velocities. $\square$ the (θ, θ) case; $\bullet$ the $(\theta, -\theta)$ case. The curves are fits to Eq. (20). The difference between the two curves is proportional to the coherence contribution u . Clearly u is velocity dependent.

per collision velocity. However, one observes large differences between the $(++)$ and the $(+-)$ case, the $(++)$ yielding a 3 to 4 times higher ion signal.

Finally, in Fig. 9 we show two measurements for the case of excitation of atom 2 with π polarized light at an angle θ , and atom 1 by σ^+ polarized light. Also shown is the fit to Eq. (27). The $\sin 2\theta$ term manifests itself by a shift of the maximum away from $\theta = 0^\circ$, since

$$R_0^{(\theta,+)} + R_1^{(\theta,+)} \cos 2\theta + R_3^{(\theta,+)} \sin 2\theta = R_0^{(\theta,+)} + R_1'^{(\theta,+)} \cos 2(\theta - \theta_0) \quad (28)$$

with

$$\begin{aligned} R_1 &= R_1' \cos 2\theta_0, \\ R_3 &= R_1' \sin 2\theta_0. \end{aligned} \quad (29)$$

As can be seen in Fig. 9 the $\sin 2\theta$ term is clearly present in the signal, its amplitude even changing sign. This amplitude is proportional to a linear combination of the coherence terms λ and μ [Eq. (27)].

FIG. 8. Polarization dependence measurement for the cases $\square$ $(\theta, 0^\circ)$ and $\bullet$ $(\theta, 90^\circ)$. The curves are fits to Eq. (20), with $R_2 = 0$.

B. Results

The information we can obtain from the measurements is basically contained in the different sets of Fourier coefficients, which are available as a function of collision velocity. Different linear combinations of the six Fourier coefficients obtained from the (θ, θ) and $(\theta, -\theta)$ measurements are shown in Fig. 10. Figure 10(A) shows three averages of everytime two Fourier coefficients. As can be seen from Eq. (21), these three averages only depend on the diagonal terms p , s , and t and on the coherence term v . Figure 10(B) shows the three differences of the same pairs of Fourier coefficients. The difference $R_0^{(\theta,\theta)} - R_0^{(\theta,-\theta)}$ should be equal to $-(R_2^{(\theta,\theta)} - R_2^{(\theta,-\theta)})$, which is the case within the error bars. These differences are proportional to the coherence term u . The considerable scattering of the experimental points in Fig. 10(B) is caused by a systematic difference between the two series of measurements we performed. Con-

FIG. 9. Polarization dependence measurements for the case $(\theta, +)$ at two different collision velocities. The curves are fits to Eq. (27). The shift of the maximum of the curves is proportional to a linear combination of the coherence terms λ and μ . This shift is clearly velocity dependent.

FIG. 10. The averages and differences of the Fourier coefficients obtained from the $(\theta, \pm \theta)$ measurements as a function of collision velocity. (A) The averages of every two Fourier coefficients. These averages depend only on the diagonal terms p , s , and t , and on the coherence term v . (B) The differences of the same three pairs of Fourier coefficients. Two of them are proportional to the coherence term u , one of them is zero within the error bars, as it should. The dashed curves in A) are the results of the fit procedure to Eq. (31) [or Eq. (33), since both the fit procedures give the same fit curves]. The ordinate scales have the dimension $[I^2]$, and from now onwards, all ordinates are in the same "arbitrary units."

sidering the fact that these points are small differences between two large numbers [cf. Fig. 10(A)] the discrepancy between the two different measurement series may be caused by, e.g., a small misalignment of the $\lambda/4$ plate. However, both measurements clearly have the same trend.

The difference $R_1^{(\theta, \theta)} - R_1^{(\theta, -\theta)}$ is indeed zero within the error bars. The dashed curves in Fig. 10(A) will be discussed later.

Figure 11 shows the four Fourier coefficients obtained from the $(\theta, 0^\circ)$ and $(\theta, 90^\circ)$ measurements. They depend only on p , s , t , and v .

Figure 12 contains the signals from the $++$ and $+-$ measurements, as well as their average (again only dependent on p , s , t , and v) and their difference. This difference, according to Eq. (26) is proportional to a linear combination of four coherence contributions.

Figure 13 shows the three Fourier coefficients of the

FIG. 11. The four Fourier coefficients obtained from the $(\theta, 0^\circ)$ and $(\theta, 90^\circ)$ measurements as a function of collision velocity. The four coefficients only depend on the diagonal terms p , s , and t and on the coherence term v . The dashed curves are the results of the fit procedure to Eq. (31).

$(\theta, +)$ measurements. Again, $R_0^{(\theta, +)}$ and $R_1^{(\theta, +)}$ only depend on p , s , t , and v , whereas $R_2^{(\theta, +)}$ is proportional to a linear combination of the coherence terms λ and μ .

It is worthwhile noting that starting from Fig. 10, all ordinates are given in the same "arbitrary units," with the dimension $[I^2]$. Uncertainties of the different experiments with respect to each other are estimated to be $\approx 5\%$. Although we did not aim at measuring absolute cross sections, we can estimate that 100 "arb. units" correspond to roughly $1 \text{ \AA}^2$ (within a factor of 2). This estimate is based on the oven temperatures, laser spot size and irradiance, and detection efficiency of our channeltron system. The value compares favorably with all values quoted and discussed by Bezuglov *et al.*⁴¹ (the average collision velocities in the cell experiments being 900–1000 m/s), except for the value of de Jong and van der Valk,¹ which is likely to be far too small.

FIG. 12. The normalized signals from the $++$ and $+-$ measurements, their average, and their difference, as a function of collision velocity. The average depends only on p , s , t , and v , the difference on a linear combination of four coherence terms. The dashed curve is the result for the average of the fit procedure to Eq. (31).

FIG. 13. The three Fourier coefficients, resulting from the $(\theta, +)$ measurements, as a function of collision velocity. Two of them depend on p , s , t , and v , the third is proportional to a linear combination of the coherence terms λ and μ . The two dashed curves are the results of the fit procedure to Eq. (31). There is a discrepancy between the $R_0^{(\theta, +)}$ coefficient and the fit at lower collision velocities.

FIG. 14. The results of our measurements in the L picture. (A) The three cross sections $\bar{\sigma}_{11}$ (average of σ_{11} and σ_{1-1}), σ_{10} , and σ_{00} as a function of collision velocity. The σ_{00} is by far the largest one. There is no significant velocity dependence visible. (B) The coherence terms v_L , u_L , r_L , and λ_L as a function of collision velocity. Three of them are velocity dependent. The magnitude of the coherence contributions is comparable with the cross sections.

V. DATA ANALYSIS

Our measurements have resulted in a total of ten coefficients, only depending on p , s , t , and v , and three others, depending on u , a linear combination of λ and μ , and a linear combination of four coherence contributions, respectively. In order to analyze the data in terms of cross sections and coherence terms, we have to choose between the L picture for our description, in which we assume that electron spin influences are negligible, and the J picture. Although the comparison of the electron spin precession time (3×10^{-13} s) and collision time ($\approx 5 \times 10^{-13}$ s at 1500 m/s) shows that it is not at all obvious that the L picture is valid, it is certainly worth the try, because in the L picture we are able to calculate all eight independent elements of the detection matrix G . Because of that the results may give a direct indication whether or not use of the L picture is justified (e.g., by yielding a negative cross section).

In the L picture, p_L , s_L , and t_L are related to the cross sections $\bar{\sigma}_{11}$, σ_{10} , and σ_{00} according to Eq. (17). When we use the stationary state values of the c_k [for our nonstationary state conditions the c_2 for the π case has to be replaced by $c_0/Q\sqrt{2}$, with Q defined in Eq. (8)] we get the following relations between the ten coefficients and the quantities $\bar{\sigma}_{11}$, σ_{10} , σ_{00} , and v_L :

$$\begin{pmatrix} R_0^{(\theta, \theta)} - R_0^{(\theta, -\theta)} \\ R_2^{(\theta, \theta)} - R_2^{(\theta, -\theta)} \\ R^{++} - R^{+-} \\ R_3^{(\theta, +)} \end{pmatrix} = \frac{1}{18} \begin{pmatrix} -1 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & -18 & 0 \\ 0 & 0 & -3 \end{pmatrix} \begin{pmatrix} u \\ r \\ \lambda \end{pmatrix}, \quad (30)$$

$$\begin{pmatrix} (R_0^{(\theta, \theta)} + R_0^{(\theta, -\theta)})/2 \\ (R_1^{(\theta, \theta)} + R_1^{(\theta, -\theta)})/2 \\ (R_2^{(\theta, \theta)} + R_2^{(\theta, -\theta)})/2 \\ R_0^{(\theta, 0^\circ)} \\ R_1^{(\theta, 0^\circ)} \\ R_0^{(\theta, 90^\circ)} \\ R_1^{(\theta, 90^\circ)} \\ (R^{++} + R^{+-})/2 \\ R_0^{(\theta, +)} \\ R_1^{(\theta, +)} \end{pmatrix} = \frac{1}{1296} \begin{pmatrix} 502 & 580 & 214 & 27 \\ -264 & 96 & 168 & -36 \\ 18 & -36 & 18 & 9 \\ 352 & 664 & 280 & 0 \\ -96 & -24 & 120 & 0 \\ 616 & 568 & 112 & 36 \\ -168 & 120 & 48 & -36 \\ 324 & 648 & 324 & 162 \\ 396 & 648 & 252 & 54 \\ -108 & 0 & 108 & -54 \end{pmatrix} \begin{pmatrix} \bar{\sigma}_{11} \\ \sigma_{10} \\ \sigma_{00} \\ v_L \end{pmatrix}. \quad (31)$$

We look for a set of cross sections $\sigma_{MM'}$ and coherence terms, which via Eqs. (30) and (31) yields the best agree-

ment with the experimentally determined R coefficients. The coherence contributions r_L and λ_L depend on one coefficient and u_L depends on the average of two, so they can be calculated directly. The three cross sections and v_L , however, have to be determined from an overdetermined set of coefficients, so we make use of the least-squares-fit technique, and perform a fit to Eq. (31). Therefore we divide our collision velocity range into zones with a width of 50 m/s, and fit the ten R coefficients to Eq. (31) in each zone. This gives us values for the cross sections and v_L in each zone, as well as the fit values for the ten R coefficients. The quality of these fits gives a good indication of the reliability of the results, since the fits would show any discrepancies between the different R coefficients. The fit values, connected with dashed lines, are shown in Figs. 10–13. In general, agreement is very good. The fact that the fit curves are no smooth lines, but instead show small fluctuations has no physical meaning. Only in the low velocity part of the fit to $R_0^{(\theta,+)}$ (Fig. 13), the fit quality is rather poor. This is caused by a discrepancy between the $R_0^{(\theta,+)}$ coefficient and the $(R^{(++)} + R^{(+-)})/2$ (Fig. 12) in this part of the velocity range. To get an idea of how far this can influence our results, we forced the fit procedure to fit the $R_0^{(\theta,+)}$ correctly. This caused a huge deviation ($\approx$ a factor of 2) between the fit and the R coefficient in Fig. 12 and a smaller deviation between the fit and the $R_1^{(\theta,+)}$ coefficient. However, there was hardly any change in the fit curves in Figs. 10 and 11, and also the results for the cross sections σ_{00} and σ_{10} were hardly affected. Only the results for $\bar{\sigma}_{11}$ and v_L changed considerably in the low velocity region. Since the results of this forced fit were far from realistic, we also performed forced fits that showed a smaller disagreement between fit values and the R coefficient in Fig. 12. The results of these fits showed that the systematic errors in $\bar{\sigma}_{11}$ and v_L caused by the discrepancy were smaller than the error bars. The results for the cross sections are shown in Fig. 14(A), the results for the coherence contributions in Fig. 14(B). In Fig. 14(A) [and in Fig. 14(B) for v_L] the calculated values (every 50 m/s) are connected with lines. The error bars of some of the calculated values are shown as well.

Up to now we have not completely determined the L -picture G matrix, we could determine only the average value $\bar{\sigma}_{11} = (\sigma_{11} + \sigma_{1-1})/2$, because the $M_L = +1$ and M_L

FIG. 15. The cross sections σ_{11} and σ_{1-1} as a function of collision velocity. Clearly, σ_{11} is significantly negative for most of our collision velocity range. This means that the L picture cannot be applied for this velocity range.

$= -1$ magnetic sublevels have the same population for all cases. The ratio of these two populations, denoted as $(M_L = +1)/(M_L = -1)$, however, can be substantially changed by introducing a weak magnetic field perpendicular to both the laser beam and atomic beam direction, when using σ light for the excitation process.³⁴ Measurements presented there provide us with information about the difference $\sigma_{11} - \sigma_{1-1} = q_L$ in the same arbitrary units we use in this section ($\pm 5\%$). Combining this q_L from Ref. 34 with our $\bar{\sigma}_{11}$, we get σ_{11} and σ_{1-1} separately, as shown in Fig. 15. It appears that σ_{11} is significantly *negative* for most of the collision velocity range. This shows that electron spin effects are important in our collision velocity range. This is not too surprising in view of the already mentioned relation between electron spin precession time and collision time. Only at our highest velocities is the collision time about equal to the precession time, the range in which normally the L picture starts to become valid.

So, in order to describe the associative ionization process properly, we have to take influences of the electron spin into account and use the J picture. Equations (30) and (31) then become

$$\begin{pmatrix} R_0^{(\theta,\theta)} - R_0^{(\theta,-\theta)} \\ R_2^{(\theta,\theta)} - R_2^{(\theta,-\theta)} \\ R^{++} - R^{+-} \\ R_3^{(\theta,+)} \end{pmatrix} = \begin{pmatrix} -\frac{1}{27} & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{27} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{9}{10} & -\frac{5}{8} & -\frac{3}{80} & \frac{3}{20}\sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{20}\sqrt{15} & -\frac{1}{80}\sqrt{10} \end{pmatrix} \begin{pmatrix} u \\ r \\ o' \\ z \\ x \\ \lambda \\ \mu \end{pmatrix}, \quad (32)$$

$$\begin{pmatrix} (R_0^{(\theta,\theta)} + R_0^{(\theta,-\theta)})/2 \\ (R_1^{(\theta,\theta)} + R_1^{(\theta,-\theta)})/2 \\ (R_2^{(\theta,\theta)} + R_2^{(\theta,-\theta)})/2 \\ R_0^{(\theta,0^\circ)} \\ R_1^{(\theta,0^\circ)} \\ R_0^{(\theta,90^\circ)} \\ R_1^{(\theta,90^\circ)} \\ (R^{++} + R^{+-})/2 \\ R_0^{(\theta,+)} \\ R_1^{(\theta,+)} \end{pmatrix} = \frac{1}{288} \begin{pmatrix} 59 & 122 & 107 & 9 \\ -60 & -24 & 84 & -12 \\ 9 & -18 & 9 & 3 \\ 20 & 128 & 140 & 0 \\ -12 & -48 & 60 & 0 \\ 80 & 152 & 56 & 12 \\ -24 & -24 & 48 & -12 \\ 18 & 108 & 162 & 54 \\ 30 & 132 & 126 & 18 \\ -18 & -36 & 54 & -18 \end{pmatrix} \begin{pmatrix} \bar{\sigma}_{3/2\ 3/2} \\ \bar{\sigma}_{3/2\ 1/2} \\ \bar{\sigma}_{1/2\ 1/2} \\ v_J \end{pmatrix} \quad (33)$$

via a least-squares-fit procedure, similar to the one described before, we can get the cross sections $\bar{\sigma}_{1/2\ 1/2}$, $\bar{\sigma}_{1/2\ 3/2}$, $\bar{\sigma}_{3/2\ 3/2}$, and the coherence term v_J . Furthermore, we also can get the coherence contribution u_J , but instead of λ_L we get a linear combination of λ_J and μ_J , and instead of r_L we get a linear combination of four coherence contributions. Out of Eqs. (30)–(33) the following equations can be deduced:

$$\begin{aligned} \bar{\sigma}_{3/2\ 3/2} &= \bar{\sigma}_{11}, \\ \bar{\sigma}_{3/2\ 1/2} &= \frac{2}{3}\sigma_{10} + \frac{1}{3}\bar{\sigma}_{11}, \\ \bar{\sigma}_{1/2\ 1/2} &= \frac{4}{3}\sigma_{00} + \frac{4}{3}\sigma_{10} + \frac{1}{3}\bar{\sigma}_{11}, \\ u_J &= \frac{2}{3}u_L, \quad v_J = \frac{2}{3}v_L. \end{aligned} \quad (34)$$

Figure 16 shows the cross sections in the J picture.

Although, in principle, the magnetic field dependence in Ref. 34 contains additional information, we would need a five parameter fit to the experimental data. Since agreement between experiment and theory is only moderate, this is in practice not possible.

VI. DISCUSSION

A. Influence of coherence contributions

To compare our present results to the earlier obtained ones, in which we had to neglect coherence contributions, we reproduce in Fig. 17 the results in the J picture of Ref. 6 with

FIG. 16. The three average cross sections $\bar{\sigma}_{1/2\ 1/2}$, $\bar{\sigma}_{3/2\ 1/2}$, and $\bar{\sigma}_{3/2\ 3/2}$ in the J picture.

the ordinate in the same scale as in Figs. 10–16.⁴⁶ We see that neglecting the coherence terms is not allowed when evaluating $\bar{\sigma}_{3/2\ 1/2}$ and $\bar{\sigma}_{3/2\ 3/2}$: both their magnitudes and shapes have drastically changed. This is to be expected, since most of the coherence contributions are larger than these two cross sections, and most of them change significantly with collision velocity.

The value of $\bar{\sigma}_{1/2\ 1/2}$ on the other hand is (above ≈ 1000 m/s) hardly changed by the coherence terms analysis. Below 1000 m/s there are significant differences. These are not caused by coherence influences but rather by the fact that in Fig. 17 we measured at detuning frequencies down to ≈ 30 MHz, which is questionable (see Sec. II D) and by the fact that we had additional information about the values of the cross sections at 250 m/s due to single beam collisions. Since we cannot excite two colliding atoms within one beam differently, we cannot use this additional information in the present analysis. However, if we assume that also at low collision velocities the $\bar{\sigma}_{1/2\ 1/2}$ value is hardly affected by the neglect of the coherence contributions u_J and v_J (which may be small at 250 m/s anyway, judging from the extrapolation of our results) the $\bar{\sigma}_{1/2\ 1/2}$ value will again be about 200 arb. units, as given in Fig. 17.

FIG. 17. The results for the three average cross sections $\bar{\sigma}_{1/2\ 1/2}$, $\bar{\sigma}_{3/2\ 1/2}$, and $\bar{\sigma}_{3/2\ 3/2}$, from an analysis in which we had to neglect coherence contributions (reproduced from Ref. 6, Fig. 5).

Generally speaking, we have shown that coherence contributions can become important and that they in general cannot be neglected.

Wang *et al.*^{8,11} also performed polarization and velocity dependent cross section measurements. If we take the difference in geometry into account, and apply our theoretical description to their data, their results do not seriously disagree with ours. Unfortunately we cannot use them to extract additional parameters, because the results of their two sets of measurements are not on the same scale.

Detailed polarization and velocity dependent associative ionization studies have also been performed on the $K(4p) + K(4p)$ system.²⁷ Apart from cross section variations due to the threshold [the energy of the minimum in the K_2^+ potential curve lies ≈ 300 meV higher than $2 \times$ the $K(4p)$ energy] and due to the opening of the $K^+ + K^-$ exit channel, which is reached in their experiments, there is a striking similarity with our results in the polarization dependence.

B. Molecular potential curves

The ultimate goal of detailed collision experiments with polarized collision partners is to be able to interpret the experimental results in a quantitative way in terms of molecular potential curves. Then one learns general facts about fundamental mechanisms governing associative ionization collisions.

In the case of the $Na(3p) + Na(3p)$ potential curves, there is a set of recent adiabatic curves available.¹⁹ However, only one of these curves crosses into the continuum, at an energy higher than available in our experiment. Furthermore Weiner⁴² has shown that the ionization process is at least partly exothermic, i.e., at least one of the potential curves leading to associative ionization crosses the Na_2^+ potential at an energy below $2 \times$ the $Na(3p)$ energy. So we have to use some kind of diabatic potential curve(s). The study of how to properly define these diabatic curves using the quantum defect method is still in progress.⁴³ Therefore, a discussion in these terms has to be postponed until further progress has been achieved.

In the mean time we can look at our preparation of the atoms at infinite distances, and assume that this preparation with respect to the internuclear axis is conserved up to very small internuclear distances, i.e., we assume a very large "locking radius." This is not unreasonable in view of the rotational analysis of the Na_2^+ molecular ion performed by Wang *et al.*⁹ which indicates a locking radius of the order of 25 Å.

Since our $+ +$ preparation, with the total angular momentum of both atoms directed along the laser propagation direction, is the most favorable one for ion production (see Fig. 12), we conclude that a $^3\Sigma$ molecular state with respect to the relative collision velocity is important for the associative ionization process.

Another way of analyzing the results lies in the use of the cross sections. The average cross section $\bar{\sigma}_{1/2, 1/2}$ is hardly smaller than the $R^+ + +$ "cross section" (cf. Figs. 12 and 16). If $\sigma_{1/2, 1/2}$ would differ considerably from $\sigma_{1/2 - 1/2}$, this

would mean that one of these two geometries is most favorable for the associative ionization, i.e., the major axis of the charge cloud points along the internuclear axis.

Our conclusions so far are in accordance with the results of the theoretical work by Jones and Dahler.^{20,21} However, their analysis was limited in the sense that they had to rely on older and less complete experimental results and potential curves. Extension of their theoretical study to the cases of Table III and our new data would be highly desirable.

VII. CONCLUDING REMARKS

We have demonstrated a detection scheme for possible complete analysis of detection matrices, which is certainly not restricted to our case study of $Na(3p) + Na(3p)$. In fact, the latter system is not the best choice, since it turns out that in the collision velocity range we use, the L picture is not valid (because the electron spins do not stay fixed in space during the collision). This means that we have to use the J picture, in which the detection matrix contains 16 independent parameters, more than can be determined experimentally.

A better case study can be obtained by repeating the $Na(3p) + Na(3p)$ experiments at higher velocities. However, a complication might be that then the $Na^+ - Na^-$ exit channel will be accessible. Another possibility, which in addition would reduce the number of potential curves involved, would be a $^1P-^1P$ system, e.g., $Ba(6s6p) + Ba(6s6p)$.

Concerning $Na(3p) + Na(3p)$, energy spectra of the ejected electrons or detailed study of the important energy pooling processes (which have much larger cross sections and may be competitive with or precedent to associative ionization) would certainly contribute to the understanding of this collision system. As to the electron spectra, preliminary experiments have been performed in Kaiserslautern, in a single beam experiment. We have studied the electron spectra when exciting the Na atoms with circularly polarized light, and with linearly polarized light with the polarization vector parallel or perpendicular to the atomic beam direction. The experimental conditions regarding the excitation process were comparable to the Utrecht situation.³⁵

Apart from the differences in the total cross sections, which reproduced very well, there was no polarization dependence visible in the electron spectrum: we saw a very narrow peak with its maximum at 0 ± 10 meV, and a width hardly exceeding the resolution of the spectrometer (40 meV). This narrow peak is in contrast with electron spectra measurements of Carré *et al.*^{2,3} They observe a broad structure which consists of a large peak at ≈ 80 meV and a smaller one at 0 meV. Both peaks are attributed by the authors to the associative ionization of two $Na(3p)$ atoms. However, preliminary experiments in Kaiserslautern,⁴⁴ in which we excited $3p$ atoms into the $7s$ level by means of a second laser show that the peak at higher energy is due to associative ionization of atoms at higher energy levels (e.g., $4d, 5p, 6s$) with ground state atoms. The higher excited atoms are formed in the experiment of Carré *et al.* too, by means of energy pooling. This mechanism is so important in their experiments because of

the relatively high Na density (more than 1000 times as high as in our experiments).

Electron spectra with better statistics will be presented and discussed in forthcoming publications.⁴⁵

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- ⁴⁶An erratum should be given here: in Ref. 6 the ordinates of several figures were also chosen such that 100 arb. units $\approx 1 \text{ Å}^2$. However, where we explicitly mentioned the absolute value of the isotropic cross section we made a mistake of a factor of 2. The isotropic cross section, as one can see from Fig. 17, is about $1.6 \times 10^{-16} \text{ cm}^2$, in good agreement, as say, with Ref. 41.