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Description of polarization-dependent associative ionization of radiatively excited atoms

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We analyze the dependence of the rate of associative ionization of two radiatively excited atoms on the polarization properties of the exciting light. This provides a direct relation between the observed ion-production rate as a function of the polarization and the ionization rates for various combinations of the magnetic substates. We consider an atomic beam irradiated by a single laser beam, as well as an atomic vapor. The description applies to a recent experimental observation of a strong polarization dependence of the ionization rate in an atomic beam, and at the same time we suggest alternate experimental methods of analyzing the total cross sections of any inelastic or reactive binary collision of excited atoms as a function of the magnetic quantum numbers.

I. INTRODUCTION

A detailed understanding of ionization processes involving excited atoms is important in astrophysics, in plasma physics, and in atomic-collision physics. When the excited atoms are produced by laser radiation, one must distinguish various possible ionization mechanisms, in particular multiphoton ionization and collisional ion production.[1] In the latter case the laser light can serve merely to prepare the excited states prior to the collision,[2-4] or the radiation can actually induce or enhance the ionization rates.[5-9] These two cases can easily be distinguished by observing the variation of the ion production rates with the laser intensity.

In the present paper we restrict ourselves to purely collisional associative ionization, according to the reaction equation

$$A^* + B^* \rightarrow (AB)^+ + e \ , \tag{1.1}$$

where the atomic species A and B may or may not be identical. This process is the source of $Na_2{}^+$ ions in a thermal sodium beam when a weak laser is tuned over the Na $3P$ resonances, as has been shown by de Jong and van der Valk.[2] In this situation the excited atoms A^* and B^* are of the same species, and the relative velocity has subthermal values. Recently,[10] we have studied the same process as a function of the direction of the linear polarization vector of the laser beam that prepared the excited sodium atoms. The ion production rate was observed to increase by a factor of 1.7 when the light polarization was rotated from a perpendicular to a parallel direction with respect to the beam direction. Obviously, this polarization dependence of the ion production reflects a dependence of the cross section for associative ionization on the magnetic quantum numbers of the excited atoms prior to the collision. The precise relation between the M-dependent cross sections and the observed polarization dependence is, however, less than trivial. In the present paper we intend to elucidate this relation by analyzing the general expression for the total cross section for any inelastic or reactive collision with initially polarized states of the collision partners. The resulting expressions suggest a well-defined set of measurements needed for a complete determination of the parameters that fix the rate constant for any pair of initial magnetic substates, both in a single atomic beam, and in a vapor cell.

II. THE IONIZATION SIGNAL

We consider the ionization process (1.1), where the excited atoms A^* and B^* before the collision are prepared in states with electronic angular momenta J_A and J_B. The most detailed theoretical quantities describing the associative ionization are the scattering amplitudes

$$f(\alpha \vec{v}_f \leftarrow M_A M_B \vec{v}_0) \ ,$$

where M_A and M_B are the initial electronic magnetic quantum numbers of the two atoms, $\vec{v}_0$ is the initial relative velocity, $\vec{v}_f$ is the final relative velocity of the ejected electron, and α indicates the relevant

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(but unobserved) quantum numbers of the molecular ion after the reaction. The initial states of the two collision partners are generally described by the density matrices ρ_A and ρ_B, defined by requiring that $\langle M_A \,|\, \rho_A \,|\, M_A \rangle$ ($\langle M_B \,|\, \rho_B \,|\, M_B \rangle$) be the density of atoms A (B) in the magnetic substate $|J_A M_A\rangle$ ($|J_B M_B\rangle$). For the case of collisions between identical atoms we obviously have to take $\rho_A = \rho_B$. Then the ion-production rate per unit volume can be expressed in the form

$$R = \int d\Omega_f \sum_{\alpha} \sum_{M_A M_A'} \sum_{M_B M_B'} [f(\alpha \vec{v}_f \leftarrow M_A M_B \vec{v}_0) f^*(\alpha \vec{v}_f \leftarrow M_A' M_B' \vec{v}_0)(m v_f/\mu)]_{\text{av}} \times \langle M_A \,|\, \rho_A \,|\, M_A' \rangle \langle M_B \,|\, \rho_B \,|\, M_B' \rangle \;, \qquad (2.1)$$

where Ω_f indicates the direction of the final relative velocity $\vec{v}_f$, m is the electron mass, and μ is the reduced mass of the two initial collision partners. The average indicated in (2.1) is taken over the distribution of the relative velocity $\vec{v}_0$ before the collision. The integration over the direction of the ejected electron and the summation over the final quantum numbers α of the molecular ion clearly correspond to the detection mode that all formed ions or electrons are detected, irrespective of the final state. In order to apply symmetry considerations, it is advantageous to express the ion production rate in the form

$$R = \mathrm{Tr}_A \mathrm{Tr}_B G \rho_A \rho_B \;, \qquad (2.2)$$

where G is a detection operator acting on the magnetic substates of the initial states of both atoms, defined by the specification of its matrix elements according to the relation

$$\langle M_A' M_B' \,|\, G \,|\, M_A M_B \rangle = \int d\Omega_f \sum_{\alpha} [f(\alpha \vec{v}_f \leftarrow M_A M_B \vec{v}_0) f^*(\alpha \vec{v}_f \leftarrow M_A' M_B' \vec{v}_0)(m v_f/\mu)]_{\text{av}} \;. \qquad (2.3)$$

As a result of the detection mode, the symmetry properties of the detection operator G merely reflect the symmetry character of the initial-velocity distribution. For any given velocity distribution, the operator G contains all the information that can possibly be obtained from a measurement of the ion production rate. In order to extract this information completely, an appropriate set of measurements is needed where, in each measurement, the initial-state density matrices act as a sieve which determines the piece of information gained.

We analyze the information content of G in the case of a single atomic beam and in the case of a vapor cell. The analysis is by no means restricted to the case of associative ionization, but it applies to any binary-collision process where the total rate of formation of the reaction products is detected. A different treatment of total reaction cross sections of initially oriented particles has been given by Okunevich.[11] We expand both the detection operator G and the two density matrices in irreducible spherical tensors T_{kq}, which obey the same rotational transformation properties as the spherical harmonics Y_{kq}.[12] The definition and some relevant properties of spherical tensors are given in Appendix A. The tensors $T_{kq}(A)$ with $0 \le k \le 2J_A$, $-k \le q \le k$, form a complete orthonormal set of operators on the $(2J_A+1)$-dimensional manifold of substates $|J_A M_A\rangle$, and we write

$$\rho_A = \sum_{kq} a_{kq} T_{kq}^{\dagger}(A) \qquad (2.4)$$

with

$$a_{kq} = \mathrm{Tr}_a \rho_A T_{kq}(A) \;. \qquad (2.5)$$

The numbers a_{kq}, which determine ρ_A completely, may be regarded as multipole coefficients of the atomic state. Likewise we expand

$$\rho_B = \sum_{kq} b_{kq} T_{kq}^{\dagger}(B) \qquad (2.6)$$

with

$$b_{kq} = \mathrm{Tr}_B \rho_B T_{kq}(B) \;. \qquad (2.7)$$

After substituting the expansions (2.4) and (2.6) in (2.2), we obtain a corresponding expansion of the ion-production rate

$$R = \sum_{kq} \sum_{k'q'} g(kq;k'q') a_{kq} b_{k'q'} \;, \qquad (2.8)$$

where the set of coefficients g as defined by

$$g(kq;k'q') = \mathrm{Tr}_A \mathrm{Tr}_B G T_{kq}^{\dagger}(A) T_{k'q'}^{\dagger}(B) \qquad (2.9)$$

determines the detection operator G completely. When the initial states $|J_A\rangle$ and $|J_B\rangle$ of the collision partners are prepared by laser excitation, the multipole coefficients a_{kq} and $b_{k'q'}$ are determined by the polarization properties of the excitation radiation. For each specific case, Eq. (2.8) equates the observed signal to an appropriate linear combination of the expansion coefficients g. The number of independent coefficients g depends on the symmetry properties of G, which in turn are mainly determined by the distribution of the relative velocities.

III. SINGLE ATOMIC BEAM

We consider the case of associative ionization of two identical atoms in a single atomic beam with an axially symmetric distribution of the relative velocity. The initial state $|J_A\rangle$ and $|J_B\rangle$ of the collision partners are taken to be the same excited state of two identical atoms. This situation corresponds to our recent experiment.[10] The number of independent parameters determining the detection operator G is now restricted by four symmetry relations. As the most natural quantization axis we choose the beam axis. As a result of rotational invariance of G for rotation about this axis, G is diagonal in the quantum number for the z component of the total electronic angular momentum of the collision partners. Hence

$$\langle M_A' M_B' \,|\, G \,|\, M_A M_B\rangle = 0$$

for

$$M_A' + M_B' \neq M_A + M_B \; . \tag{3.1}$$

Furthermore, G is invariant for reflection about any plane through the beam axis. If we select the xz plane, this means that G is invariant under the combined action of space inversion and rotation over π about the y axis. This leads to the relation

$$\langle M_A' M_B' \,|\, G \,|\, M_A M_B\rangle = (-)^{M_A' + M_B' - M_A - M_B}\langle -M_A' - M_B' \,|\, G \,|\, -M_A - M_B\rangle \; . \tag{3.2}$$

Because of the identity of the initial states of both atoms, G must be invariant for an interchange on both sides of the two states. Hence we obtain

$$\langle M_A' M_B' \,|\, G \,|\, M_A M_B\rangle = \langle M_B' M_A' \,|\, G \,|\, M_B M_A\rangle \; . \tag{3.3}$$

Finally, by definition G is a Hermitian operator, obeying the relation

$$\langle M_A' M_B' \,|\, G \,|\, M_A M_B\rangle = \langle M_A M_B \,|\, G \,|\, M_A' M_B'\rangle^* \; . \tag{3.4}$$

By using the properties of the spherical tensors T_{kq} as mentioned in Appendix A, it is a simple matter to convert the symmetry properties (3.1)–(3.4) into relations for the expansion coefficients g. We find

$$g(kq;k'q') = 0, \quad \text{for } q + q' \neq 0 \tag{3.5}$$

$$g(kq;k'q') = (-)^{k-q+k'-q'} g(k\;-q;k'\;-q') \; , \tag{3.6}$$

$$g(kq;k'q') = g(k'q';kq) \; , \tag{3.7}$$

$$g(kq;k'q') = (-)^{q+q'} g^*(k\;-q;k'\;-q') \; . \tag{3.8}$$

From this set of symmetry relations the number of independent parameters determining G can be found. For a certain pair of values k, k' of the ranks of the multipoles with $k \le k'$, the number of parameters is $k+1$ for $k+k'$ even, and k for $k+k'$ odd. [Note that $g(k0;k'0) = 0$ for odd values of $k+k'$, as a result of (3.6).] Both multipole ranks k and k' can attain integer values from zero up to $2J_A = 2J_B$. For integer values the number of independent parameters determining G is equal to

$$(J_A+1)(4J_A^2+5J_A+3)/3 \; ,$$

and for half-integer values this number amounts to

$$(2J_A+1)(8J_A^2+14J_A+9)/12 \; .$$

When the initial excited state of the atoms in the beam is prepared by laser irradiation, there is normally a quantization axis for which the density matrix of these excited atoms is diagonal. For excitation with linearly polarized light this axis coincides with the direction of the linear polarization vector, and for circularly polarized light this quantization axis is determined by the laser beam direction. The spherical tensors with respect to this quantization axis are called t_{kq}, and when $\rho_A = \rho_B$ is expanded in t_{kq}, only components with $q=0$ appear, according to the equation

$$\rho_A = \rho_B = \sum_k c_k t_{k0}^{\dagger} \; . \tag{3.9}$$

For various excitation conditions explicit expressions for the expansion coefficients c_k can be obtained with standard techniques, while accounting for possible saturation effects and hyperfine coupling. A summary of the pertaining formalism is given in Appendix B.

For given properties of the exciting radiation we wish to obtain an expression for the ion-production rate R as a function of the angle θ between the laser-dependent quantization axis and the z axis, which coincides with the atomic-beam direction. When we choose the x and y direction in such a way that the laser-dependent quantization axis lies in the xz plane, the relation between the tensors t_{kq} and T_{kq} is given by the transformation rules

$$t_{k0}=\sum_{q} T_{kq}d^{k}_{q0}(\theta)\ , \tag{3.10}$$

where $d^{k}_{qq'}$ are the reduced rotation matrices[13] that define the transformation properties of the spherical harmonics Y_{kq} or the spherical tensors T_{kq} under a rotation about the y axis. Substitution of (3.10) into (3.9) yields an explicit expression of the expansion coefficients $a_{kq}=b_{kq}$ as a function of the angle θ between the laser-dependent quantization axis and the z axis. The resulting expression for the θ-dependent ion production rate is

$$R(\theta)=\sum_{kq}\sum_{k'q'} g(kq;k'q')c_k c_{k'} d^{k}_{q0}(\theta)d^{k'}_{q'0}(\theta)\ . \tag{3.11}$$

The coefficients c_k should be known from the excitation conditions, and a comparison of (3.11) with experiment gives direct information on the coefficients g determining the detection operator G. The real reduced rotation matrices d^{k}_{q0} are simply related to the spherical harmonics by the relation[13]

$$e^{-i\phi q}d^{k}_{q0}(\theta)=[4\pi/(2k+1)]^{1/2}Y^{*}_{kq}(\theta,\phi)\ . \tag{3.12}$$

From the symmetry relations

$$\begin{aligned} d^{k}_{q0}(\theta)&=(-)^{q}d^{k}_{q0}(-\theta)=(-)^{k-q}d^{k}_{q0}(\pi-\theta)\\ &=(-)^{q}d^{k}_{-q0}(\theta) \end{aligned} \tag{3.13}$$

one finds that $R(\theta)$ obeys the identity

$$R(\theta)=R(-\theta)=R(\pi-\theta)\ . \tag{3.14}$$

Hence we can expand R as a Fourier series

$$R(\theta)=\sum_{n=0}^{2J_A} R_n\cos(2n\theta)\ . \tag{3.15}$$

The upper limit $n=2J_A$ in the Fourier expansion (3.15) follows from the definition of the reduced rotation matrices d^{k}_{q0} which cannot have higher Fourier components than $\exp(\pm ik\theta)$. The number of parameters that can be determined from $R(\theta)$ for a certain excitation mode is therefore at most $2J_A+1$. For excitation with linearly polarized light, only coefficients c_k with even value of k occur in the expansion (2.9), and the highest k value is not $2J_A$, but $2J_A-1$ for half-integer values of J_A. Hence in this special case of linear polarization of the exciting light and a half-integer J_A value, the number of parameters obtained from a measurement of $R(\theta)$ is no more than $2J_A$. A subsequent measurement of $R(\theta)$ with excitation by circularly polarized light would provide us with another set of $2J_A+1$ measured parameters. A change of right-circular polarization to left-circular polarization would multiply c_k with $(-)^k$. One readily finds that $R(\theta)$ is not affected by this change, and that no additional information is obtained.

Not all parameters $g(kq;k'q')$ can be detected from the signal (3.11). From the symmetry relation (3.6) and (3.13) it is obvious that the coefficients $g(kq;k'q')$ with odd values of $k+k'$ do not contribute to the ionization rate. Furthermore, when the excited atoms are prepared by absorption of linearly polarized light, the multipole coefficients c_k can only be nonzero for even k values, so that in this case only the coefficients $g(kq;k'q')$ with even values of k and k' contribute to (3.11). On the other hand, all coefficients $g(kq;k'q')$ would contribute to the ionization rate when the exciting radiation has an elliptical polarization that is not purely circular or linear.

We shall now illustrate these general considerations in some specific cases. The Fourier coefficients R_n can be directly related to the parameters c_k and g by writing the products $d^{k}_{q0}d^{k'}_{q'0}$ as an analogous Fourier series. We consider the case that the multipole coefficients c_k of the initial excited state are nonzero only for $k=0$, 1, 2. This covers the case of unsaturated excitation of any transition, and also the case of saturated excitation of a state with $J_A=J_B\le 1$, as well as the case of saturated excitation of a state with $J_A=J_B=\frac{3}{2}$ with linearly polarized light. We introduce the abbreviated notation for the relevant independent expansion coefficients $g(kq;k'q')$

$$\begin{aligned} &g(0\,0;0\,0)=p\ ,\\ &g(1\,0;1\,0)=q,\ \ g(1\,1;1\,-1)=r\ ,\\ &g(2\,0;0\,0)=s\ ,\\ &g(2\,0;2\,0)=t,\ \ g(2\,1;2\,-1)=u\ ,\\ &g(2\,2;2\,-2)=v\ . \end{aligned} \tag{3.16}$$

Then the ion-production rate is given by the Fourier expansion (3.15) with three coefficients R_0, R_1, and R_2, which obey the explicit equations

$$R_0 = c_0^2 p + \tfrac{1}{2} c_1^2 (q - r) + \tfrac{1}{2} c_0 c_2 s + c_2^2 (11t - 12u + 9v)/32 \ , \tag{3.17}$$

$$R_1 = \tfrac{1}{2} c_1^2 (q + r) + \tfrac{3}{2} c_0 c_2 s + 3 c_2^2 (t - v)/8 \ , \tag{3.18}$$

$$R_2 = c_2^2 (9t + 12u + 3v)/32 \ . \tag{3.19}$$

When multipole moments c_k with $k > 2$ are also present, we have to add terms containing these higher moments to (3.17)–(3.19), and also higher Fourier amplitudes R_n with $n \le k$ arise in the expansion (3.15).

A. $J_A = J_B = \frac{1}{2}$

In this special case only multipole terms with $k = 0$ or 1 can be supported by the excited state, and the only unknown parameters are p, q, and r. When the excited atoms are prepared by absorption of linearly polarized light, the excited state is isotropic, and we can write

$$c_0 = n_e/\sqrt{2}, \quad c_1 = 0 \ . \tag{3.20}$$

The ionization signal is then obviously independent of θ, and we find

$$R_0 = n_e^2 p/2, \quad R_1 = 0 \ . \tag{3.21}$$

By exciting the atoms with circularly polarized light, one often only populates the substate with the angular momentum component $M = \frac{1}{2}$ in the direction of the light beam, corresponding to the multipole coefficient

$$c_0 = c_1 = n_e/\sqrt{2} \ , \tag{3.22}$$

which leads to the Fourier amplitudes

$$R_0 = n_e^2 [\tfrac{1}{2} p + \tfrac{1}{4} (q - r)] \ ; \qquad R_1 = \tfrac{1}{4} n_e^2 (q + r) \ . \tag{3.23}$$

A determination of these coefficients (3.21) and (3.23) in these two cases completely determines the expansion coefficients p, q, and r, and thereby the three independent matrix elements of G

$$\begin{aligned} \langle \tfrac{1}{2}\ \tfrac{1}{2} \,|\, G \,|\, \tfrac{1}{2}\ \tfrac{1}{2} \rangle &= (p + q)/2 \ , \\ \langle \tfrac{1}{2}\ {-\tfrac{1}{2}} \,|\, G \,|\, \tfrac{1}{2}\ {-\tfrac{1}{2}} \rangle &= (p - q)/2 \ , \\ \langle \tfrac{1}{2}\ {-\tfrac{1}{2}} \,|\, G \,|\, {-\tfrac{1}{2}}\ \tfrac{1}{2} \rangle &= -r \ . \end{aligned} \tag{3.24}$$

B. $J_A = J_B = 1$

In this case of $J = 1$, the detection operator G is fully specified by eight independent parameters, namely the seven coefficients (3.16), and the imaginary coefficient $g(2\ 1;1\ -1)$, which does not contribute to the ion-production rate (3.11). The seven parameters (3.16) can be fully determined from a measurement of $R(\theta)$ in several excitation modes. When the state is excited by absorption of linearly polarized light driving the transition from a lower state with $J = 0$ to this excited state, then only the state with angular momentum component $M = 0$ along the polarization direction is populated. This corresponds to the values of the multipole moments

$$c_0 = n_e/\sqrt{3}, \quad c_1 = 0 \ , \qquad c_2 = -n_e \sqrt{2/3} \ . \tag{3.25}$$

Another independent excitation mode occurs when the same transition is driven by unpolarized light. Then the excited-state density matrix is

$$\rho_A = \rho_B = \tfrac{1}{2} n_e (\,|\, 1 \rangle \langle 1 \,|\, + \,|\, -1 \rangle \langle -1 \,|\,) \tag{3.26}$$

with the light-beam direction as quantization axis. The corresponding values of the multipole moments are

$$c_0 = n_e/\sqrt{3}, \quad c_1 = 0 \ , \qquad c_2 = n_e/\sqrt{6} \ . \tag{3.27}$$

Successive substitution of these values (3.25) and (3.27) in (3.17)–(3.19) gives rise to six linear equations for the five unknown parameters p, s, t, u, and v. (Note that the occurrence of q and r is suppressed for $c_1 = 0$.) Five of these six equations are linearly independent. Hence the measurement of $R(\theta)$ in these two cases of excitation by linearly polarized light (where θ is the angle between the polarization direction and the atomic beam) and by unpolarized light (where θ is the angle between the light beam and the atomic beam) is sufficient for a full determination of these five parameters. If the ion-production rate is also measured with excitation of right circularly polarized light, the initial excited density matrix is

$$\rho_A = n_e \,|\, 1 \rangle \langle 1 \,|\, \ ,$$

and the multipole moments are

$$c_0 = n_e/\sqrt{3}, \quad c_1 = n_e/\sqrt{2} \ , \qquad c_2 = n_e/\sqrt{6} \tag{3.28}$$

with the quantization axis in the light-beam direction. Substitution of (3.28) in (3.17)–(3.19) yields another set of three linear equations containing all seven parameters (3.16). One verifies that these equations are sufficient to calculate p, q, r, s, t, u, and v from a measurement of $R(\theta)$ in these three cases. Then also, G is known apart from the imaginary part $\mathrm{Im}\langle 1\ -1\,|\,G\,|\,0\ 0\rangle$, which is equal to the expansion coefficient $ig(2\ 1;1\ -1)$. This coefficient can be determined by a measurement of R after excitation with elliptically polarized light. We shall not give further details of the analysis. For any specific case it can be carried out by the method outlined in this paper. The relation between the expansion coefficients (3.16) and the matrix elements of G is easily found from the definition (2.9).

C. Larger values of J_A and J_B

The coefficients $g(k0;k'0)$ are linear combinations of the diagonal matrix elements (2.3) of G, where $M_A'=M_A$ and $M_B'=M_B$. These diagonal elements

$$\langle M_AM_B\,|\,G\,|\,M_AM_B\rangle = K(M_AM_B) \tag{3.29}$$

are the rates of associative ionization of atom pairs in the magnetic substates $|J_AM_A\rangle$ and $|J_BM_B\rangle$ with the atomic-beam direction as quantization axis. The integrand in (2.3) is positive definite in this case, whereas in the off-diagonal case $M_A'\neq M_A$ and $M_B'\neq M_B$, the integrand is a product of two different complex amplitudes, which can be positive as well as negative. If the phases of these amplitudes vary sufficiently rapidly with the direction of $\vec{v}_f$, the off-diagonal elements of G are expected to be small compared to the diagonal ones. If we boldly neglect the off-diagonal elements altogether, the number of remaining unknown parameters $g(k0;k'0)$ would be greatly reduced. It is precisely this assumption that we adopted for the interpretation of the observed ion-production rate $R(\theta)$ of excited Na in an excited state with $J_A=J_B=\frac{3}{2}$.[10] Furthermore, the exciting light was linearly polarized so that only the multipole coefficients c_k with even k could be nonzero. The only three remaining unknown parameters contributing to the signal $R(\theta)$ were p, s, and t, which are related to the specific ionization rates by the identities valid for $J_A=J_B=\frac{3}{2}$,

$$\begin{aligned} p &= A+2B+C\ ,\\ s &= A-B\ ,\\ t &= A-2B+C \end{aligned} \tag{3.30}$$

with

$$\begin{aligned} A &= \tfrac{1}{2}[K(\tfrac{3}{2}\ \tfrac{3}{2})+K(\tfrac{3}{2}\ -\tfrac{3}{2})]\ ,\\ B &= \tfrac{1}{2}[K(\tfrac{3}{2}\ \tfrac{1}{2})+K(\tfrac{3}{2}\ -\tfrac{1}{2})]\ ,\\ C &= \tfrac{1}{2}[K(\tfrac{1}{2}\ \tfrac{1}{2})+K(\tfrac{1}{2}\ -\tfrac{1}{2})]\ . \end{aligned} \tag{3.31}$$

In the excitation mode which we used, by driving with linearly polarized light the transition between the hyperfine sublevels $F=2\rightarrow F=3$ of the

$$\mathrm{Na}(3S_{1/2}\rightarrow 3P_{3/2})$$

transition, the relative populations of the substates with $|M_A|=\frac{3}{2},\frac{1}{2}$ are 1:5, which means that the multipole coefficients are

$$\begin{aligned} &c_0=n_e/2,\quad c_1=0\ ,\\ &c_2=-n_e/3,\quad c_3=0\ . \end{aligned} \tag{3.32}$$

Substitution of (3.30)–(3.32) in (3.17)–(3.19) gives the relation between the three measurable Fourier amplitudes R_0, R_1, R_2 and the three quantities A, B, and C. One notices that we were not able to distinguish substates with opposite magnetic quantum number $\pm M$, owing to the use of linearly polarized exciting light.

Here we point out that more information can be obtained on the specific rates $K(M_AM_B)$ by measuring, in addition, the ion production $R(\theta)$ as a function of the angle θ between the atomic beam and the light beam, while using successively circularly polarized light, unpolarized light, and elliptically polarized light. In principle, all the 16 independent matrix elements of G can be determined in this manner.

It will by now be obvious that nothing precludes the generalization of this analysis to associative ionization of initial excited states with even higher values of the electronic angular momentum. If the ionization rate is independent of the initial magnetic substates, the only nonzero expansion coefficient of G would be $g(0\ 0;0\ 0)$. A nonzero value of any coefficient $g(kq;k'q')$ with $k\neq 0$ or $k'\neq 0$ is a measure for the M dependence of the rate of associative ionization.

IV. ATOMIC VAPOR

In the previous section we have seen in detail how a dependence of the associative-ionization rate on the initial magnetic quantum number gives rise to a dependence of the ion-production rate on the polarization of the radiation that excites the initial state.

We shall now point out that effects of this dependence can also be observed in an isotropic medium, such as a vapor cell. Then the detection operator G, as defined in (2.3), is invariant for rotations of the pair of collision partners. This means that the expansion coefficient $g(kq;k'q')$ is proportional to the Clebsch-Gordan coefficient

$$\langle kq;k'q' \,|\, 0\,0\rangle \;,$$

indicating that the two anisotropies of both partners can only be recoupled to an overall tensor of rank zero. This is equivalent to the statement that G is diagonal in the total electronic angular momentum of the partners A and B combined. We parametrize G by writing for the expansion coefficient the relations

$$g(kq;k'q')=\delta_{kk'}\delta_{q\,-q'}(-)^q g_k \;, \tag{4.1}$$

where the Kronecker delta's force k and k' to be equal, and q to be the opposite of q'. The number of independent real parameters g_k determining G completely is equal to the minimum of $2J_A+1$ and $2J_B+1$, and the value of each one of these parameters is all that one can possibly extract from observation of polarization-dependent ion-production rates.

A. Binary gas mixture

We consider a dilute mixture of two gases of the atoms A and B, and we assume that associative ionization can occur when two atoms collide in initially excited states with angular momenta J_A and J_B. The excited states of the two species are prepared by irradiation with two lasers, so that their polarization properties can be chosen independent of one another. One will notice that the total ion production may include the ions $A_2{}^+$ and $B_2{}^+$ as well as the ions AB^+ which we are interested in. The background of the homonuclear ions can be independently determined by performing measurements with only either one of the lasers switched on.

We assume that both lasers are linearly or circularly polarized. Then the density matrix of the excited atoms of both species are diagonal with respect to a properly chosen quantization axis, determined by the polarization direction or the laser beam direction for linear and circular polarization, respectively. However the quantization axes of both species can be independently selected, and we call θ the angle between these two axes. The multipole coefficients of each excited state with respect to its own quantization axis are denoted as a_k and b_k, analogous to Eq. (3.9). Before we can apply the general result (2.8) for the ion-production rate, we first have to relate the multipole expansions of both atoms to a single quantization axis. This can be done by applying a rotation over an angle θ about the axis perpendicular to both quantization axes, giving rise to a rotation matrix element[13]

$$d^k_{00}(\theta)=P_k(\cos\theta) \;, \tag{4.2}$$

where P_k indicates a Legendre polynomial. The resulting expression for the ion-production rate R as a function of the angle θ takes the simple form

$$R(\theta)=\sum_k a_k b_k g_k P_k(\cos\theta) \;. \tag{4.3}$$

Since the Legendre polynomials are a complete set of functions, the parameters g_k can be determined from a measurement of R for each value of k for which both a_k and b_k are nonzero. After saturated excitation with circularly polarized light, this is usually the case for all k values from zero up to the minimum of $2J_A+1$ and $2J_B+1$. Hence a measurement of $R(\theta)$ as a function of the angle θ between the two circularly polarized laser beams is usually sufficient for a complete determination of the detection operator G. The relation between the parameters $g_k=g(k0;k0)$ and the ionization rates $K(M_AM_B)$ is easily found by applying Eq. (2.9). If these rates are all equal, the parameters g_k for $k>0$ vanish, and R becomes independent of θ. In this isotropic system the rates $K(M_AM_B)$ are usually not independent, since these $(2J_A+1)(2J_B+1)$ quantities are all determined by the parameters g_k.

B. Pure gas

Finally, we consider associative ionization of identical laser-excited atoms in a pure gas, where both collision partners are now excited by a single laser beam. The initial excited state has electronic angular momentum $J_A=J_B$. Obviously, changing the direction of the incident laser beam cannot alter the total ion-production rate in this isotropic system. However we wish to point out that the ion-production rate does depend on the polarization properties of the exciting radiation. When the excited-state density matrix is diagonal with respect to some quantization axis (as is the case for linear or circular polarized radiation and in the case of unpolarized light), we can introduce the multipole moments c_k of the excited state of both partners in analogy to (3.9). The ion-production rate then takes the form

$$R=\sum_k c_k^2 g_k \ , \tag{4.4}$$

which is just a special case of (4.3) for $\theta=0$. When the exciting radiation is elliptically polarized, we have to include multipole coefficients $a_{kq}=b_{kq}$ with $q\neq 0$, and the general expression for the rate R is found after substitution of (4.1) in (2.8)

$$R=\sum_{kq} |a_{kq}|^2 g_k \ , \tag{4.5}$$

where we used

$$a_{kq}^*=(-)^q a_{k-q} \ ,$$

due to the hermiticity of $\rho_A=\rho_B$. The independent parameters g_k can be determined provided that one performs measurements of R in a sufficient number of different polarizations. Obviously, this number must be larger for larger values of the angular momentum $J_A=J_B$.

V. CONCLUSIONS

We have analyzed the polarization dependence of the rate of associative ionization of laser-excited atoms in several cases. In the first case a single laser beam resonantly excites identical atoms in a single atomic beam. A measurement of the ion-production rate as a function of the polarization vector of the light or of the laser-beam direction can then give complete information on the ionization rate for any combination of magnetic substates. This analysis is given in Sec. III, and it is directly applicable for the description of our recent experiment[10] on the associative ionization of excited sodium atoms. Furthermore, we consider in Sec. IV the case of a vapor cell. For a gas mixture both atomic species can be excited by a different laser beam with an independently chosen direction and polarization, which provides a method of investigating the dependence of the ionization rate for various combinations of magnetic substates. Finally, we consider a pure gas, excited by a single laser beam. Then the direction of the laser beam cannot affect the total ion-production rate, but this rate is affected by the choice of the polarization of the laser. It is therefore essential to specify the polarization property of the exciting light when providing data on experimentally determined associative-ionization cross sections.[4]

The formalism presented in this paper is in no way restricted to the case of associative ionization, but it is applicable to analyze the polarization dependence of the total rate of any inelastic or reactive binary collision.

APPENDIX A: SPHERICAL TENSORS

We give some relevant definitions and properties of spherical tensorial sets.[12,13] Density matrices of an atomic state with angular momentum J can be represented as a $(2J+1)$-dimensional matrix. It is often convenient to expand a density matrix in spherical tensors $T_{kq}(J)$, which are defined by the explicit expression for their matrix elements

$$\langle JM\,|\,T_{kq}(J)\,|\,JM'\rangle =(-)^{J-M'}\langle JM;J\ -M'\,|\,kq\rangle \ , \tag{A1}$$

where k and q can attain the values $k=0, 1, \ldots, 2J$, $q=-k, -k+1, \ldots, k$. The rotational transformation properties of the spherical tensorial set T_{kq} for a fixed value of k are the same as those of the spherical harmonics Y_{kq}. The tensors T_{kq} form a complete orthonormal basis, as indicated by

$$\mathrm{Tr}T_{kq}^\dagger(J)T_{k'q'}(J)=\delta_{kk'}\delta_{qq'} \ , \tag{A2}$$

and every density matrix can be expressed as a linear combination of these tensors, according to the relation

$$\rho=\sum_{kq} a_{kq}T_{kq}^\dagger(J) \ \text{with}\ a_{kq}=\mathrm{Tr}\rho T_{kq}(J) \ . \tag{A3}$$

Furthermore, the tensors obey the relation

$$T_{kq}^\dagger(J)=(-)^q T_{k-q}(J) \ , \tag{A4}$$

and a Hermitian density matrix has multipole coefficients obeying the identity

$$a_{kq}^*=(-)^q a_{k-q} \ . \tag{A5}$$

It often occurs that an excited state of an atom is prepared by irradiating a certain hyperfine transition, and the density matrix is conveniently expressed as an expansion in the spherical tensors $T_{kq}(F)$, where F is the total angular momentum of the excited hyperfine sublevel. If this excited state serves as the initial state for a certain inelastic collision process, it is usually fully justified to assume that this collision is not affected by the nuclear spin. Then it is convenient to reduce the expansion in $T_{kq}(F)$ into an expansion in $T_{kq}(J)$ by taking a partial trace over the nuclear spin I. This partial trace obeys the identity[13]

$$\mathrm{Tr}_I T_{kq}(F) = (-)^{J+F+k+I}(2F+1) \times \begin{Bmatrix} J & J & k \\ F & F & I \end{Bmatrix} T_{kq}(J) \; . \qquad \text{(A6)}$$

This equation can be applied to obtain an expansion of the reduced density matrix $\mathrm{Tr}_I\rho$ in tensors $T_{kq}(J)$, from an expansion in tensors $T_{kq}(F)$ of the full density matrix ρ for nuclear and electronic angular momentum states.

Transition operators coupling an initial state with angular momentum J' to a final state with angular momentum J can likewise be expanded in terms of spherical tensors coupling these states, defined by their matrix elements

$$\langle JM \mid T_{kq}(JJ') \mid J'M' \rangle = (-)^{J'-M'} \times \langle JM; J' \; -M' \mid kq \rangle \; . \qquad \text{(A7)}$$

Let us consider a transition dipole operator $\vec{\mu}^{(+)}$, coupling the lower state $\mid J' \rangle$ to an upper state $\mid J \rangle$. According to the Wigner-Eckart theorem,[12,13] the spherical components of this dipole operator are simply proportional to the spherical tensors of rank 1, and we write

$$\vec{\mu}^{+} \cdot \vec{u}_\sigma = \langle J || \mu || J' \rangle T_{1\sigma}(JJ')/\sqrt{3} \; , \qquad \text{(A8)}$$

where $\langle J || \mu || J' \rangle$ is a reduced matrix element that determines the strength of the dipole transition. The spherical unit vectors $\vec{u}_\sigma$ for $\sigma = 0, \pm 1$ are defined by the equation

$$\vec{u}_{\pm 1} = (\mp \hat{x} - i\hat{y})/\sqrt{2}, \quad \vec{u}_0 = \hat{z} \; , \qquad \text{(A9)}$$

where $\hat{x}$, $\hat{y}$, $\hat{z}$ are the unit vectors in the x, y, z direction. Note that radiation propagating in the z direction with right circular polarization has $\vec{u}_1$ as its polarization vector, and the polarization vector $\vec{u}_0$ corresponds to light that is linearly polarized in the z direction.

APPENDIX B: STATIONARY EXCITED STATE

The rate equations determining the density matrices of an upper state and a lower state coupled by polarized light are well known.[14,15] When the polarization vector of the radiation is equal to any one of the spherical unit vectors $\vec{u}_\sigma$, it is sufficient to consider the populations of the magnetic substates of each level. We consider the transition between two isolated states with angular momenta F' and F, irradiated with light with polarization vector $\vec{u}_\sigma$. Stimulated transitions only couple an excited state $\mid FM \rangle$ to a lower state $\mid F'M - \sigma \rangle$, and spontaneous decay couples the state $\mid FM \rangle$ to the lower states $\mid F'M' \rangle$ with $M' = M$, $M \pm 1$. The stimulated transition rate $\Gamma(M; M - \sigma)$ between the upper substate $\mid FM \rangle$ and the lower substate $\mid F'M - \sigma \rangle$ is

$$\Gamma(M; M - \sigma) = 3 \, | \langle FM \mid F'M - \sigma; 1\sigma \rangle |^2 \times B(F \to F')P \; , \qquad \text{(B1)}$$

where $B(F \to F')$ is the Einstein coefficient for stimulated emission, and P is the spectral intensity of the laser radiation at resonance. The spontaneous transition rate $A(M; M')$ from the state $\mid FM \rangle$ to the state $\mid F'M' \rangle$ obeys the equation

$$A(M; M') = | \langle FM \mid F'M'; 1M \; -M' \rangle |^2 A \; , \qquad \text{(B2)}$$

where A is the Einstein coefficient for spontaneous decay. If we denote the upper-state populations as N_M and the lower-state ones as $n_{M'}$, then the rate equations for the populations are

$$\begin{aligned} \dot{N}_M &= -AN_M - \Gamma(M; M - \sigma)(N_M - n_{M-\sigma}) \; , \\ \dot{n}_{M'} &= \sum_M A(M; M')N_M + \Gamma(M' + \sigma; M') \times (N_{M'+\sigma} - n_{M'}) \; . \end{aligned} \qquad \text{(B3)}$$

In the stationary limit the ratio of N_M and $n_{M-\sigma}$ is determined by the relation

$$\Gamma(M; M - \sigma) n_{M-\sigma} = [A + \Gamma(M; M - \sigma)] N_M \; , \qquad \text{(B4)}$$

whereas subtraction of the two equations (B3) gives rise to the stationary-state relations[16,14]

$$N_M = \sum_{M_1} | \langle FM_1 \mid F'M - \sigma; 1M_1 - M + \sigma \rangle |^2 N_{M_1} \; . \qquad \text{(B5)}$$

Equation (B5) demonstrates that in the stationary state the ratios of the populations of the excited substates are fully determined by Clebsch-Gordan coefficients alone, irrespective of the laser intensity and the strength of the transition. If the lower state has a substate $\mid F'M' \rangle$ that is not coupled to an upper substate by stimulated transitions, then

$$\Gamma(M' + \sigma; M') = 0 \; .$$

One notices from the second equation in (B3) that all N_M are zero in the stationary limit and all the atoms are trapped in this substate of the lower level.

For circularly polarized light ($\sigma = \pm 1$) a stationary upper-state population is only possible if $F = F' + 1$, and the only populated substates are $|FM\rangle$ and $|F'M'\rangle$ with $M = \pm F$, $M' = \pm F'$, for $\sigma = \pm 1$, and the ratio of these populations is fixed by Eq. (B4). [Notice, moreover, that the relevant Clebsch-Gordan coefficient in (B1) is unity in this case.] The excited state is thus a pure state in this case.

For linearly polarized light ($\sigma = 0$) the situation is slightly more involved. For $F = F' - 1$, the excited state is not populated in the stationary limit, since the substates $|F'M'\rangle$ with $M' = \pm F'$ are not affected by the field.

For $F = F'$ where F is an integer, again there is no excited-state population in the stationary limit, since the Clebsch-Gordan coefficient

$$\langle F\,0\,|\,F\,0;1\,0\rangle = 0\ ,$$

so that $\Gamma(0;0)$ disappears. Hence in the stationary limit all atoms will end up in the lower substate $|F'0\rangle$.

The only nontrivial cases for linear polarization arise when $F = F'$ and F is a half integer, and when $F = F' + 1$. From (B5) one may derive the ratio of populations of neighboring substates, in the case that $\sigma = 0$, and one finds

$$N_M\,|\,\langle F\,M\,|\,F'M-1;1\,1\rangle\,|^2 = N_{M-1}\,|\,\langle FM-1\,|\,F'M;1-1\rangle\,|^2\ . \qquad \text{(B6)}$$

In the case that $F = F'$, the Clebsch-Gordan coefficients in (B6) are opposites of each other, and we conclude that all excited-state populations N_M are equal for excitation with linearly polarized light of a transition between two states with equal half-integer angular momenta. Then obviously the excited state is fully isotropic, and all multipole components c_k with $k > 0$ vanish.

In the case that $F = F' + 1$, the equations (B6) are solved by

$$N_M = n_e\,|\,\langle 2F-1,0\,|\,F-1,M;F,-M\rangle\,|^2 \qquad \text{(B7)}$$

as has been shown by Macek and Hertel.[14] The total excited-state population n_e depends on the laser intensity and the coupling strengths.

In each of these cases with a stationary population of the excited state (circular polarization and $F = F' + 1$, linear polarization and $F = F' =$half-integer linear polarization and $F = F' + 1$), half of the atoms populates the excited state in the saturation limit.

The multipole moments of the excited state can be directly obtained from the populations of the magnetic substates. When the states $|F\rangle$ and $|F'\rangle$ are hyperfine sublevels, the multipole expansion of the total density matrix can be reduced to the multipole expansion of the electronic state by applying Eq. (A6).

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[1] T. B. Lucatorto and T. J. McIlrath, Appl. Opt. 19, 3948 (1980).

[2] A. de Jong and F. van der Valk, J. Phys. B 12, L561 (1979).

[3] J. Weiner and P. Polak-Dingels, J. Chem. Phys. 74, 508 (1981).

[4] V. S. Kushawaha and J. J. Leventhal, Phys. Rev. A 22, 2468 (1980).

[5] A. van Hellfeld, J. Caddick, and J. Weiner, Phys. Rev. Lett. 40, 1369 (1978).

[6] J. Weiner, J. Chem. Phys. 72, 2856 (1980).

[7] P. Polak-Dingels, J. Keller, J. Weiner, J.-C. Gauthier, and N. Bras, Phys. Rev. A 24, 1107 (1981)

[8] F. Roussel, B. Carré, P. Breger, and G. Spiess, J. Phys. B 14, L313 (1981).

[9] B. Carré, F. Roussel, P. Berger, and G. Spiess, J. Phys. B 14, 4271 (1981).

[10] J. G. Kircz, R. Morgenstern, and G. Nienhuis, Phys. Rev. Lett. 48, 610 (1982).

[11] A. I. Okunevich, Zh. Eksp. Teor. Fiz. 77, 574 (1979) [Sov. Phys.—JETP 50, 290 (1979)].

[12] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic, New York, 1957).

[13] D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon, Oxford, 1967).

[14] J. Macek and I. V. Hertel, J. Phys. B 7, 2173 (1974).

[15] A. Omont, Prog. Quantum Electron. 5, 69 (1977).

[16] I. V. Hertel and W. Stoll, J. Phys. B 7, 583 (1974).