Atomic alignment effects in the associative ionization of sodium

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(Received 15 May 1990)

The individual cross sections $\sigma(m_a,m_b)$ for the associative ionization process $\mathrm{Na}(3p,m_a)+\mathrm{Na}(3p,m_b)\to\mathrm{Na_2}^+ + e$ are calculated semiclassically over a wide velocity range. Qualitative comparisons are made with experimental results in which the colliding Na(3p) atoms have been excited by laser into specific m_l states.

The associative ionization (AI) process $2\mathrm{Na}(3p)\to\mathrm{Na_2}^+ + e$ has been studied extensively in the past decade (for a recent review see Ref. 1). Most of the earlier experimental studies[2–5] have been carried out in vapor cells and have yielded only the statistically averaged cross sections. The first measurements made with an atom beam in which Na(3p) has been excited by laser into specific space-quantized substates was that of Kircz, Morgenstern, and Nienhuis,[6] and an alignment-dependent effect was observed. Since then a number of other measurements[7–11] in single or colliding beams with specific m_a and m_b initial preparation has resulted in a more detailed study of alignment effects in this AI process.

On the theoretical side, we have carried out a semiclassical calculation for this process[12] resulting in good agreement with the vapor-cell measurements[3,4] of the average cross section in the 600-K temperature range. The purpose of this paper is to present the individual cross sections for aligned atoms that are evaluated in that calculation. We will then comment on how these compare with measurements on aligned atoms.

The present calculations ignore fine-structure effects in Na, as the fine-structure splitting is a negligible perturbation on any of the diabatic or adiabatic energy curves that are relevant to the theory. Taking the quantization Z axis to lie along the relative velocity vector $\mathbf{v}$, and the YZ plane to be the collision plane, the initial diabatic states $H_{ii}(R)$, which asymptotically go to $\mathrm{Na}(3p,m_a)$ and $\mathrm{Na}(3p,m_b)$, may be extracted from doubly excited diabatic molecular-orbital energy curves evaluated by Henriet and Masnou-Seeuws.[13] The final diabatic state $H_{ff}(R)$ is taken as the sum of an existing calculated $\mathrm{Na_2}^+$ potential curve and the ejected electron energy $\varepsilon=k^2/2$. The probability of making a transition from H_{ii} to H_{ff} is evaluated at the crossing of these curves by a stationary phase method to be

$$P_{m_a m_b}=\frac{(3p|r|3s)^2}{12\pi^2}\times\int_{k_{\min}}^{k_{\max}}dk\,k\frac{G_{m_a m_b}(k)}{\left|R^6\frac{d(H_{ii}-H_{ff})}{dR}\right|_c}\left\langle\frac{1}{\left|\frac{dR}{dt}\right|_c}\right\rangle . \quad (1)$$

Here $G_{m_a m_b}$ represents the combinations of separated-atom bound-free radial matrix elements coming from the dipole-dipole coupling between the two atoms for the four independent $m_a m_b$ pairs,

$G_{m_a m_b}$	m_a	m_b
$\frac{4}{3}(3p\|r\|ks)^2+\frac{16}{15}(3p\|r\|kd)^2$	0	0
$\frac{1}{2}(3p\|r\|kd)^2$	1	0
$\frac{1}{3}(3p\|r\|ks)^2+\frac{1}{15}(3p\|r\|kd)^2$	1	1
$\frac{2}{5}(3p\|r\|kd)^2$	1	-1

(2)

We assume that the relative motion $\mathbf{R}(t)$ of the two colliding atoms follows a trajectory corresponding to the *adiabatic* molecular state which dissociates to the $m_a m_b$ initial atomic pair. These adiabatic curves have also been evaluated by Henriet and Masnou-Seeuws.[13] As there are generally several molecular adiabatic states corresponding to each $m_a m_b$ initial atom pair, we do a statistical average over these in evaluating the quantity $\langle |dR/dt|_c^{-1}\rangle$ in (1). For each ejected electron momentum k in the integrand of (1), there is a crossing radius R_c for the initial and final *diabatic* energy curves and a corresponding $[d(H_{ii}-H_{ff})]/dR_c$. The quantity $|dR_c/dt|^{-1}$, or reciprocal of the radial velocity at the diabatic crossing, depends on the adiabatic trajectory, and so we must average (including the statistical weights) that quantity over all the adiabatic potential curves corresponding to $m_a m_b$. The usual integral of $\rho^2 P_{m_a m_b}$ over impact parameter ρ completes the semiclassical evaluation of the AI cross sections $\sigma(m_a,m_b)$. By symmetry, $\sigma(-1,0)=\sigma(0,-1)=\sigma(0,1)=\sigma(1,0)$, $\sigma(-1,-1)=\sigma(1,1)$, and $\sigma(-1,1)=\sigma(1,-1)$.

The $\sigma(m_a,m_b)$ are given over an extended relative velocity range in Fig. 1. The very-low-v behavior of these is governed by the asymptotic form of the adiabatic potentials, which in this case is the quadrupole-quadrupole interaction $c_5(m_a,m_b)/R^5$. It happens that only $c_5(1,0)<0$, giving an attractive potential, so that only atoms in this channel will approach each other in an inward spiraling orbit, leading to an indefinitely increasing effective AI cross section (since the curve-crossing separation R_c will always be reached). The resulting increase in AI cross section has been observed in cold-atom measurements.[11,14] Since the other $c_5(m_a,m_b)>0$, there will be barriers to overcome in the other channels, resulting in finite threshold velocities for the AI process to set in. The high-energy cutoff, which begins to set in for $v>4000$ m/s, is due to the orbits approaching straight lines and $P_{m_a m_b}(\rho \le R_c)$ being reduced by the effective $1/v$ factor. The crossing radii of the various initial diabatic state curves with the final one are seen (from Fig. 1 in Ref. 12) to be fairly close to one another $[\sim(8-9)a_0]$, so that the differences in magnitudes of the $\sigma(m_a,m_b)$ are attributable mainly to the differences in their bound-free dipole probabilities, i.e., $G_{m_a m_b}$, and averaging over the adiabatic orbits associated with each $m_a m_b$ channel. It is clear from (2) that G_{00} is the dominant one and G_{11} is the smallest one [since $(3p|r|kd)^2>(3p|r|ks)^2$ over most of the range of k]. The other wiggles that appear in these curves are due to the specific numerics entering expression (1), and so do not allow for a detailed physical explanation. A beam study of the v dependence of the total AI cross section for 2K(4p) has been made by Brencher, Nawracala, and Pauly,[15] and it shows a high-v cutoff at $v\sim4000$ m/s, similar to what we find for 2Na(3p) in Fig. 1.

Several beam measurements[6-11] have been made for 2Na(3p) that have investigated the effects of atomic alignment on the associative ionization rate. The general procedure is to excite the Na(3p) with laser radiation perpendicular to the atom beams (Z direction) and linearly polarized at an angle θ with Z. If the probability that this excites Na(3p,m) is $w_m(\theta)$, then the resulting average AI cross section is

$$\bar{\sigma}(\theta)=\sum_{m_a,m_b} w_{m_a}(\theta)w_{m_b}(\theta)\sigma(m_a,m_b)\ . \tag{3}$$

The problem with constructing such $\bar{\sigma}(\theta)$ from theoretical $\sigma(m_a,m_b)$, or extracting "measured" $\sigma(m_a m_b)$ from a relative measurement of $\bar{\sigma}(\theta)$, is that one is completely dependent on the correctness of the $w_m(\theta)$ that are used.

For example, many of these measurements carry out the excitation using the transition $3s\,^2S_{1/2}(F=2)\rightarrow 3p\,^2P_{3/2}(F=3)$. An analysis by Hüwel, Maier, and Pauly[16] based on the stationary state m_F distribution in the upper state yields for the m_l probabilities

$$w_0=\tfrac{1}{3}(\tfrac{2}{3}+\cos^2\theta),\quad w_{\pm1}=\tfrac{1}{6}(\tfrac{7}{3}-\cos^2\theta)\ . \tag{4}$$

The AI results of Kircz, Morgenstern, and Nienhuis[6] and Rothe *et al.*[7] are in agreement and give the form of the relative signal for $\bar{\sigma}(\theta)$ as having its maximum value at $\theta=0°$ and its minimum at $\theta=90°$, with the ratio

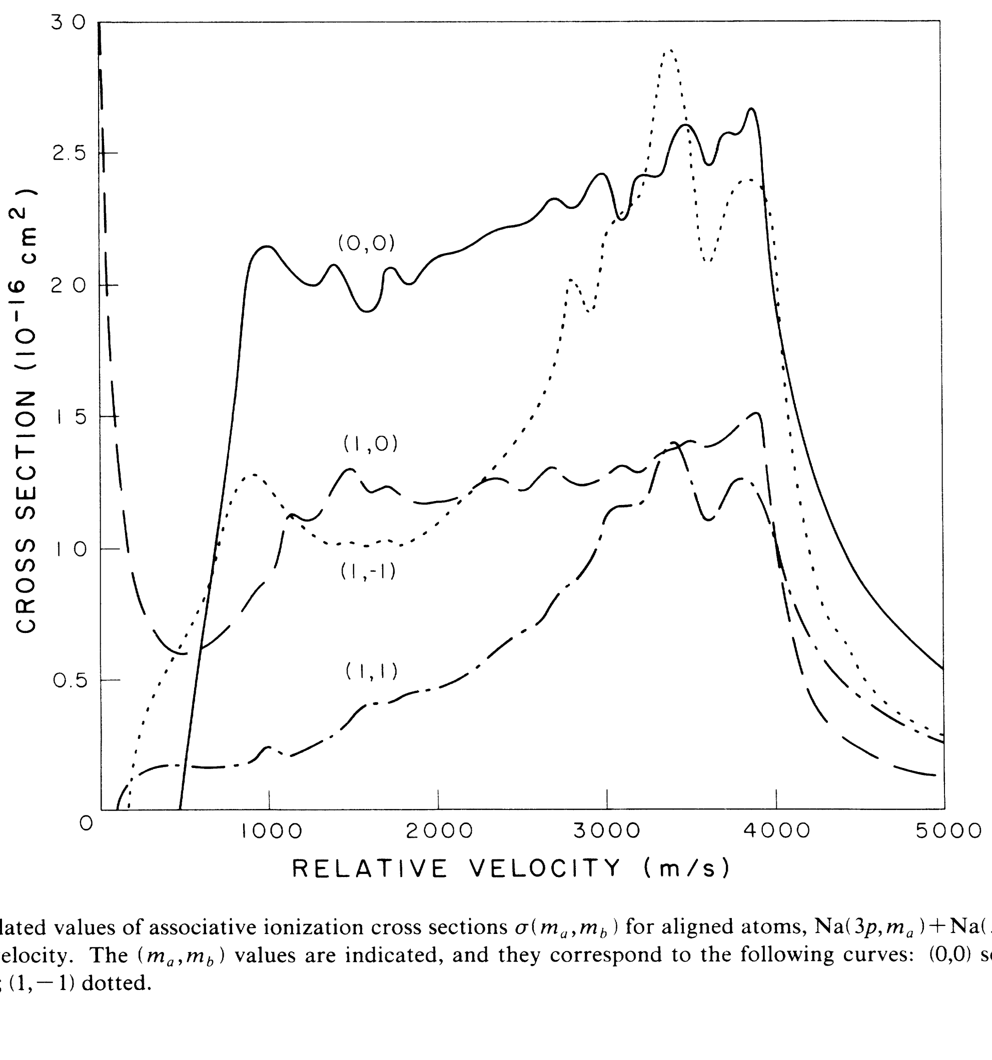

FIG. 1. Calculated values of associative ionization cross sections $\sigma(m_a,m_b)$ for aligned atoms, Na(3p,m_a)+Na(3p,m_b), as a function of relative velocity. The (m_a,m_b) values are indicated, and they correspond to the following curves: (0,0) solid; (1,0) dashed; (1,1) dash-dotted; (1,−1) dotted.

$\bar{\sigma}(0°)/\bar{\sigma}(90°)\cong 1.6$. These intrabeam collisions of excited Na($3p$) atoms correspond to a mean relative velocity of ~ 500 m/s. While this is close to our calculated threshold relative velocity for $\sigma(00)$, we obtain $\bar{\sigma}(\theta)$ also having their maximum and minimum values at 0° and 90°, respectively, for $v \gtrsim 500$ m/s. We find the $\bar{\sigma}(0°)/\bar{\sigma}(90°)$ ratios of 1.2, 1.3, 1.4, and 1.5 at velocities of 600, 800, 1000, and 1400 m/s, respectively. As the relative velocity is lowered and the various thresholds seen in Fig. 1 are crossed one would expect radical departures in the form of $\bar{\sigma}(\theta)$. At $v=300$ m/s, we find $\bar{\sigma}(\theta)$ to have a rather sharp maximum at $\sim 45°$. If one goes to $v \lesssim 100$ m/s, where only $\sigma(1,0)$ is nonvanishing, one would expect to see $\bar{\sigma}(\theta)=\frac{4}{9}(\frac{2}{3}+\cos^2\theta)(\frac{7}{3}-\cos^2\theta)\sigma(1,0)$. This has a broad maximum at 24.1°, a minimum at 90°, and $\bar{\sigma}(0°)/\bar{\sigma}(90°)=\frac{10}{7}$. An experimental test of this would be a valuable check on the validity of the present theory.

In the work of Meijer *et al.*[9,10] measurements were carried out with two colliding Na beams at many relative velocities in the range 900–2400 m/s. The atoms in each beam were excited by linearly polarized radiation with adjustable angles of polarization. In the typical measurements made at the relative velocities 1060 and 1960 m/s, data were given for identical angles of polarization (θ,θ) and for the case $(\theta,\pi-\theta)$. Since the excitation probabilities in (4) are the same for either polarization configuration we would expect identical values for $\bar{\sigma}(\theta)$. However, Meijer *et al.*[9,10] have given a detailed analysis based on the theory of Nienhuis[17] in which coherence terms are expected to give rise to different $\bar{\sigma}(\theta)$ for each of the above polarization configurations. The measurements showed no "coherence" effect at 1060 m/s and an appreciable one at 1960 m/s, and $\bar{\sigma}(0°)/\bar{\sigma}(90°)$ ratios of 1.9 and 1.7 at the two respective relative velocities. Our corresponding calculated ratios are 1.43 and 1.40. Two additional measurements by Meijer *et al.* involving linearly polarized radiation consisted of a fixed polarization (either along Z or along Y) for one beam and varying the angle θ of the polarization vector of the radiation exciting the other beam. For the measurements done at $v=1540$ m/s they found $\bar{\sigma}(0°)/\bar{\sigma}(90°)$ ratios of 1.6 and 1.1 for Z and Y fixed polarization, respectively, compared with our calculated 1.2 for both cases. Also the ratio of cross sections at $\theta=0$ was measured to be $\bar{\sigma}_Z(0°)/\bar{\sigma}_Y(0°)=1.7$, while our calculated value is 1.2.

A colliding beam measurement of Na($3p$) AI in which each beam was independently excited by radiation linearly polarized along the X, Y, or Z axis (referred to as ⊙, 8, or ∞ p-orbital orientation) was carried out by Wang *et al.*[8] as a function of relative velocity. A subsequent analysis of these data by Wang and Weiner[18] allowed them to extract the ratios $\sigma(0,0)/\sigma(1,0)$ and $\sigma(0,0)/\bar{\sigma}(1,1)$, where $\bar{\sigma}(1,1)=\frac{1}{2}[\sigma(1,1)+\sigma(1,-1)]$. These are compared with our calculated ratios in Fig. 2 of Ref. 12. The order of the agreement is roughly in the range of a factor 1.5–2. The observed predominance of $\sigma(0,0)$ over other alignment channels for $600<v<2200$ m/s is thus clearly confirmed theoretically.

In summary, we have presented the results of a semiclassical calculation for the associative ionization of aligned Na($3p$) atoms. These results are qualitatively consistent with a number of measurements carried out with various alignment configurations, and we hope they will be useful in guiding future measurements to help us obtain a fuller understanding of this process.

Partial support was provided by the National Science Foundation through Grant No. PHY86-04504, and all computations were done on the Joint Institute for Laboratory Astrophysics VAX 8600.

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