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Associative ionization in collisions of electronically excited Na atoms with vibrationally excited Na$_2$(v$''$) molecules

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Abstract. We have studied the formation of Na$_3^+$ ions in collisions of Na$(3d, 5s, 4d)$ atoms with vibrationally excited Na$_2(v'')$ molecules in their electronic ground state in a supersonic beam. The cross-section of the Na$(4d_{5/2})+$Na$_2$ associative ionization is found to be about six times larger than that of the corresponding atomic reaction Na$(4d_{5/2})+$Na$(3s) \rightarrow$ Na$_2^+$. Associative ionization in collisions of Na$(3d)$ with Na$_2(v'')$ is observed only with vibrationally excited Na$_2$ molecules. The cross-section $\sigma(v'')$ of this reaction increases only slightly with v'' for low vibrational excitation, while a strong increase with v'' is observed for $v'' \geq 26$. The latter observation suggests the opening of the channel leading to the formation of Na$_3^+$ ions in the first electronically excited state for $v'' \geq 26$.

PACS. 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states (including lifetime, state mixing, etc.) – 34.50.Fa Electronic excitation and ionization of atoms (including beam-foil excitation and ionization)

1 Introduction

Contrary to the well-known associative ionization (AI) in collisions of sodium atoms (see [1] for details and references therein) atom-molecule AI has not been studied until recently. The formation of Na$_3^+$ ions in AI has been observed for the first time in collisions of electronically excited molecules with ground-state atoms [2]:

$$\mathrm{Na_2}(2^1\Pi_g) + \mathrm{Na}(3s) \rightarrow \mathrm{Na_3^+} + \mathrm{e}\,. \qquad (1)$$

Two other studies consider AI in collisions of ground-state molecules with electronically excited atoms [3],

$$\mathrm{Na_2}(X^1\Sigma_g^+) + \mathrm{Na}(4d) \rightarrow \mathrm{Na_3^+} + \mathrm{e}\,, \qquad (2)$$

$$\mathrm{Na_2}(X^1\Sigma_g^+) + \mathrm{Na}(5s) \rightarrow \mathrm{Na_3^+} + \mathrm{e}\,, \qquad (3)$$

and in collisions of molecules and atoms excited in their first excited states [4,5]

$$\mathrm{Na_2}(A^1\Sigma_u^+) + \mathrm{Na}(3p) \rightarrow \mathrm{Na_3^+} + \mathrm{e}\,. \qquad (4)$$

The authors of [2] used process (1) as an ion source for a space-charge limited diode ionisation detector. They made no attempt to further study the formation of trimer ions. Processes (2, 3) and (4) were considered in more detail. Processes (2) and (3) were studied in an effusive beam, using time-of-flight (TOF) mass spectrometry to distinguish different ionic products. The cross-sections were determined relative to the corresponding atom-atom AI reactions

$$\mathrm{Na}(3s) + \mathrm{Na}(4d) \rightarrow \mathrm{Na_2^+} + \mathrm{e}\,, \qquad (5)$$

$$\mathrm{Na}(3s) + \mathrm{Na}(5s) \rightarrow \mathrm{Na_2^+} + \mathrm{e}\,. \qquad (6)$$

It was found that the atom-molecule AI cross-section is twice as large as the cross-section of the respective atomic reaction in case of the $4d_{5/2}$ state, and 10 times larger in case of the $5s_{1/2}$. The cross-sections for the reactions (5) and (6) have been measured in sodium vapour in an earlier study [6]. An estimate of the cross-section for the process (5) is also available, based on electron spectrometric studies in an effusive beam [7].

Process (4) was studied in a vapour cell, with excitation of the molecules to the lowest vibrational levels, $v' = 0$ and 1, in the $A^1\Sigma_u^+$ state [4]. The cross-section was estimated to be $\sigma \approx 10^{-15}$cm^2, which is an order of magnitude larger than that of the process [1]:

$$\mathrm{Na}(3p) + \mathrm{Na}(3p) \rightarrow \mathrm{Na_2^+} + \mathrm{e}\,. \qquad (7)$$

A more detailed study [5] in a supersonic beam revealed that the rate constant for the reaction (4) is essentially independent of v' at small vibrational excitation ($v' = 0 \ldots 10$), but increases significantly with v' for $v' \geq 11$. For $v' = 14$ the reaction is nearly one order of magnitude more efficient than for low v'.

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It is well known that vibrational excitation affects the cross-section for inelastic collisions [8], for atom-molecule exchange reactions [9], or for dissociative attachment of low-energy electrons to molecules [10–12]. The sensitivity of the process of charge transfer from Rydberg states to the vibrational level of the molecule has also been confirmed recently [12]. Observations of AI of ground-state Na_2 molecules with Na($3d$) atoms in a supersonic beam suggested that vibrational excitation of molecules may significantly enhance the trimer ion production rate [13]. In particular, Na_3^+ ions were observed from the process $Na(3d) + Na_2(X^1\Sigma_g^+, v'')$ only for $v'' > 0$, although the energy of the $3d$ state lies 13 meV above the Na_3 ionisation threshold.

Our present study is concerned with the consequences of the initial molecular vibrational excitation for the process of AI in collisions of Na atoms excited to their $3d$, $5s$ or $4d$ states with $Na_2(X^1\Sigma_g^+, v'')$.

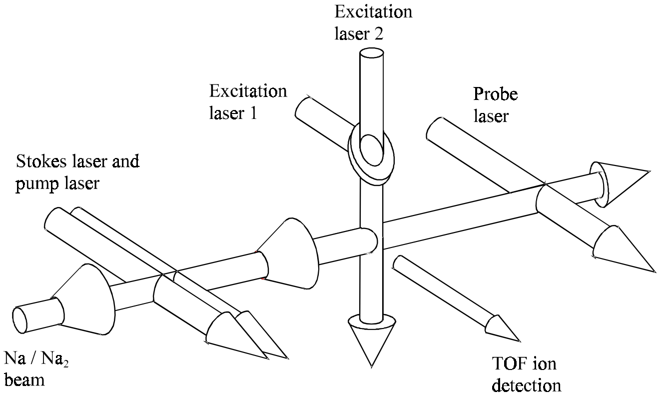

Fig. 1. Schematic arrangement of particle and laser beams. Excitation lasers 1 and 2 excite atoms in the reaction region. Only the pump laser is used for vibrational excitation via Franck-Condon pumping (FCP). Both the pump and the Stokes lasers are needed when the STIRAP method is implemented. The probe laser detects vibrational excitation of Na_2 molecules.

2 Experiment

2.1 Supersonic beam setup

The experiment is done in a single supersonic Na/Na_2 beam with TOF mass analysis to distinguish the trimer ions from Na_2^+ and Na^+ ions. The latter ions are produced in atomic associative ionization or by the process of Penning ionization. The experimental setup is described in detail in reference [11]. Briefly, the beam expands from an oven operated at 900 K temperature through a 0.4 mm diameter nozzle, the temperature of which is held 50 K higher than that of the oven. The beam is collimated by two skimmers to a divergence of about 1°, which limits the residual transverse Doppler broadening to 40 MHz. The concentrations of atoms and molecules in the reaction region 20 cm downstream from the nozzle are $n_{\mathrm{Na}} \approx 2.3 \times 10^{11}$ cm^{-3} and $n_{\mathrm{Na}_2} \approx 2 \times 10^{10}$ cm^{-3}, respectively.

In our supersonic beam, 99% of the dimers are concentrated in their lowest vibrational level, $v'' = 0$, and about 1% are found in $v'' = 1$. The maximum of the population distribution over the rotational levels is found at $J'' = 7$. This level contains about 9% of the total population. The velocity and the velocity distribution of atoms or molecules in the beam are readily measured by the Doppler shift technique [14,15]. The beam velocity is 1340 m/s, and the width of the distribution function is 300 m/s for atoms or 260 m/s for molecules (full width at $1/e$). The mean relative velocity of atom-atom or atom-molecule collisions is $v_{\mathrm{AA}} = 120$ m/s or $v_{\mathrm{MA}} = 112$ m/s, which corresponds to a mean collision energy $\overline{E}_{\mathrm{AA}} = 1.4$ meV or $\overline{E}_{\mathrm{MA}} = 1.6$ meV.

2.2 Optical preparation of atoms and molecules

The experimental arrangement of particle and laser beams is shown in Figure 1. All the lasers used in the experiment are cw single-mode ring lasers (CR-699 or CR-899) with a linewidth of about 1 MHz. Atoms are optically excited in the reaction region in $3d$, $5s$ or $4d$ states by a two-step excitation scheme. One laser drives the $3s_{1/2} \rightarrow 3p_{3/2}$ ($F'' = 2 \rightarrow F' = 3$) transition, while the other laser excites atoms from $3p_{3/2}$ to the desired higher-lying states. Radiative cascading from these states leads to the population of all hyperfine sublevels, and a loss of atoms to the $F'' = 1$ sublevel of the $3s_{1/2}$ state by optical pumping is inevitable.

One consequence of optical pumping is a variation of the location of the highest density of atoms in the excited state with laser power. When the excitation probability is small compared to unity, the density of Na* is highest near the axis of the laser beam. However, with increasing excitation probability because of increasing laser power, the region of highest Na* density moves upstream with respect to the propagation of the particles in the beam and is found in the wings of the laser beam profile [16] and thus away from the region of highest detection efficiency for the time-of-flight analysis. In order to assure the independence of the detection efficiency with regard to a variation of the laser intensity, the latter was kept sufficiently low to prevent saturation. As a test, the Na_2^+ ions from process (5) or from

$$Na(3p) + Na(5s) \rightarrow Na_2^+ + e\,, \qquad (8)$$

$$Na(3p) + Na(3d) \rightarrow Na_2^+ + e\,, \qquad (9)$$

were observed to determine the saturation limits (see Fig. 2a). At the given low collision energy in our experiment, the contribution of process (7) to the ion signal is negligibly small compared to the processes (5, 8) and (9).

To prepare vibrationally excited Na_2 molecules in their electronic ground state, either Franck-Condon pumping (FCP) [15] or stimulated Raman adiabatic passage (STIRAP) [17] is used. In the case of FCP, molecules are excited to different v' levels of the $A^1\Sigma_u^+$ state on

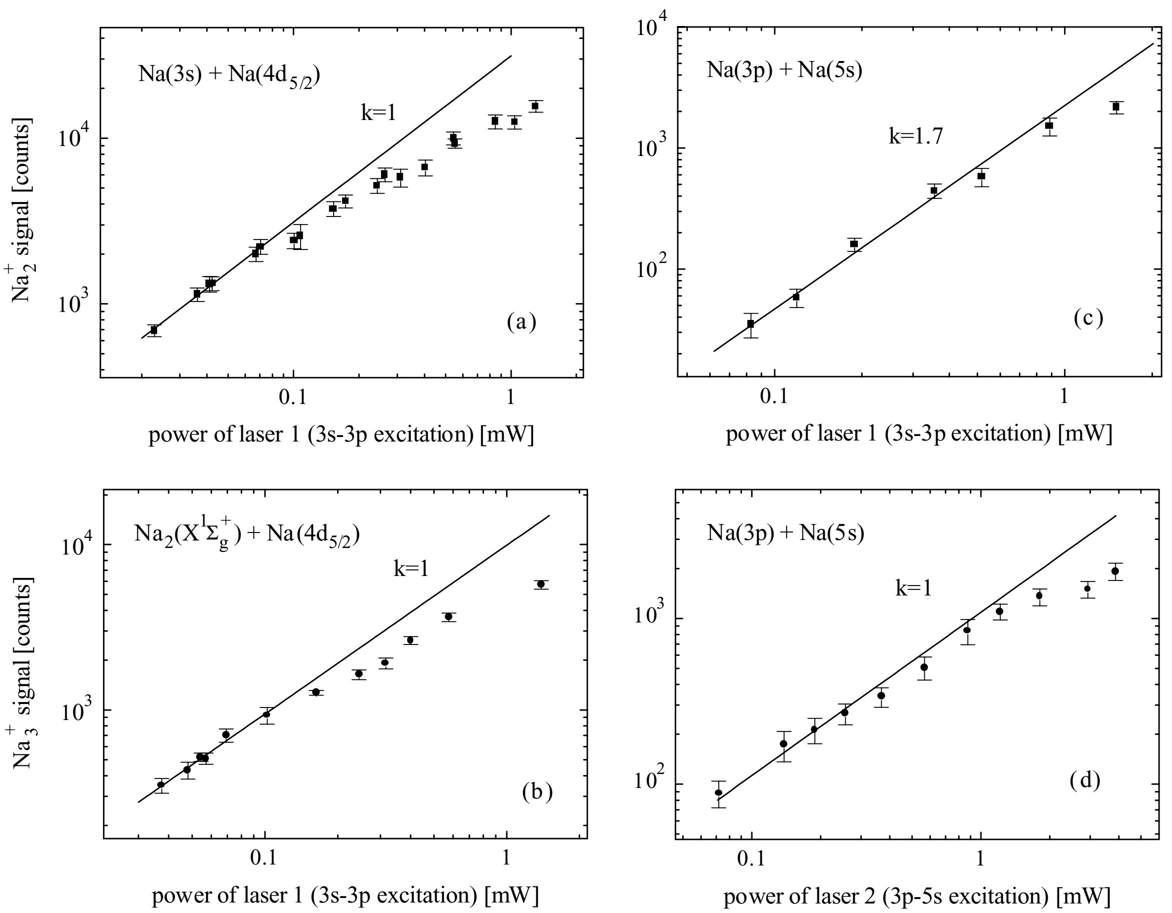

Fig. 2. Power dependence of the ion formation. Laser beams are focused to ⊘ ~ 2 mm. Saturation is indicated in (a) and (b) for the ion signals due to processes $\mathrm{Na}(3s) + \mathrm{Na}(4d) \to \mathrm{Na}_2^+ + \mathrm{e}$ and $\mathrm{Na}_2(X^1\Sigma_g^+) + \mathrm{Na}(4d) \to \mathrm{Na}_3^+ + \mathrm{e}$. Dependence of the Na_2^+ ion signal due to process $\mathrm{Na}(3p) + \mathrm{Na}(5s) \to \mathrm{Na}_2^+ + \mathrm{e}$ on the power of laser 1 is nearly quadratic (c), but linear on the power of laser 2 (d).

$A^1\Sigma_u^+(v', 10) \leftarrow X^1\Sigma_g^+(0, 9)$ transitions. Depending on v' in the electronically excited state, spontaneous decay of the molecules creates different population distributions $f_{v'}(v'')$ over vibrational levels (v'') of the $X^1\Sigma_g^+$ state (Fig. 3), which are unambiguously determined by the corresponding transition rates (which include the variation of the transition dipole moment with internuclear distance). To avoid collisions of electronically excited molecules with the excited atoms, the pump laser beam intersects the particle beam 15 cm upstream of the reaction region (see Fig. 1). With the molecular transition being saturated, FCP leads to efficient (≈ 100%) optical pumping of the molecules to the vibrationally excited levels of the molecular ground state. To verify the molecular excitation, a probe laser resonant with the $A^1\Sigma_u^+(5, 10) \leftarrow X^1\Sigma_g^+(0, 9)$ transition intersects the particle beam downstream from the reaction region. The lower (v'', J'') level is the same for pump and probe lasers. Therefore the probe-laser–induced fluorescence signal decreases whenever the pump laser is resonant with the chosen transition. This together with the wavemeter readings provides an unambiguous verification that the desired molecular transition is excited.

Contrary to the FCP, STIRAP allows one to selectively transfer the population from $v'' = 0$ to excited vibrational levels in the electronic ground state. In STIRAP, a Stokes laser field couples the intermediate $(v', 10)$ level in the $A^1\Sigma_u^+$ state with the final $(v''_f, 9)$ level in the $X^1\Sigma_g^+$ state prior to the interaction of molecules with the pump laser field, which couples the initial $(0, 9)$ and intermediate levels. The sequence of interactions is controlled by the spatial displacement of the axes of the pump and Stokes lasers [17]. With a properly adjusted displacement all the population of the initial level is transferred to the chosen final level. The lasers are detuned from the resonance with the respective molecular transitions by an equal amount of 200 MHz, maintaining the two photon resonance for the $(v'' = 0,\ J'' = 9) \to (v',\ J' = 10) \to (v''_f,\ J''_f = 9)$ transitions. The population transfer efficiency by STIRAP, which in the present experiment was reaching up to 99%, is monitored with the probe laser on $A^1\Sigma_u^+(v'_{\mathrm{pr}}, 10) \leftarrow X^1\Sigma_g^+(v''_f, 9)$ transitions.

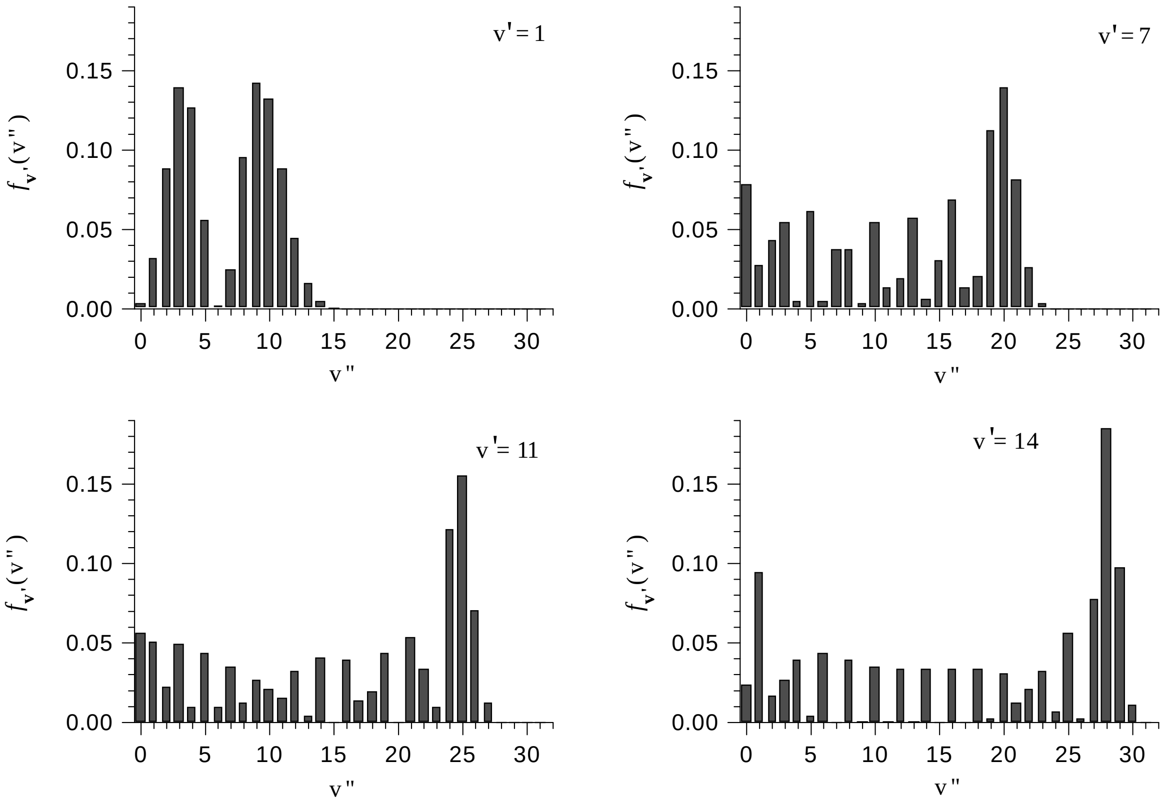

Fig. 3. Population distribution $f_{v'}(v'')$ established by Franck-Condon pumping for various v'.

3 Results and analysis

3.1 $\mathrm{Na_2}(v'') + \mathrm{Na}(4d)$ collisions

Upon excitation of the Na $4d_{3/2}$ and $4d_{5/2}$ states, Na^+, Na_2^+, and Na_3^+ ions are observed in the mass spectrum (see Fig. 4). The Na^+ ions are formed in atomic Penning and photoionization processes [7,18]:

$$\mathrm{Na}(3p,4d) + \mathrm{Na}(4d) \rightarrow \mathrm{Na}^+ + \mathrm{Na} + \mathrm{e}\,, \tag{10}$$

$$\mathrm{Na}(4d) + h\nu \rightarrow \mathrm{Na}^+ + \mathrm{e}\,. \tag{11}$$

The Na_2^+ ions are formed in atomic AI processes (5) and (7). At the low collision energies of our experiment, the process (7) is relatively inefficient, and gives about two orders of magnitude smaller contribution to the observed Na_2^+ signal than the process (5). This was verified by measuring the Na_2^+ signal with the laser beam for the $3p \rightarrow 4d$ excitation blocked, in agreement with observations by the authors of [7].

The formation of Na_3^+ ions is due to AI of $\mathrm{Na_2}(X^1\Sigma_g^+, v'')$ molecules and $\mathrm{Na}(4d)$ atoms according to process (2). The Na_3^+ signal varies linearly with the power of the laser for the $3s \rightarrow 3p$ excitation (see Fig. 2b). This confirms that one $\mathrm{Na}(4d)$ atom is needed to form Na_3^+. Since the densities of ground-state atoms and molecules are known, and $\mathrm{Na}(4d)$ atoms participate also in the formation of Na_2^+, the atom-molecule AI cross-section can be determined relative to the cross-section for the atom-atom AI process (5) [3]. The rates of production of Na_2^+ and Na_3^+ ions in the processes (5) and (2) are, respectively

$$\dot{N}_{\mathrm{Na}_2^+} = \sigma_{\mathrm{AA}} v_{\mathrm{AA}} \int n_{\mathrm{Na}} n_{\mathrm{Na}(4d)} \mathrm{d}V_{\mathrm{AA}}\,,$$

$$\dot{N}_{\mathrm{Na}_3^+} = \sigma_{\mathrm{MA}} v_{\mathrm{MA}} \int n_{\mathrm{Na}_2} n_{\mathrm{Na}(4d)} \mathrm{d}V_{\mathrm{MA}}\,,$$

where σ_{AA} and σ_{MA} are the velocity-averaged cross-sections for the reactions (5) and (2), while the densities of the ground-state atoms, ground-state molecules and excited $\mathrm{Na}(4d)$ atoms are n_{Na}, n_{Na_2}, and $n_{\mathrm{Na}(4d)}$, respectively. The reaction volumes V_{AA} and V_{MA} are identical since they are both determined by the distribution of excited $\mathrm{Na}(4d)$ atoms. Therefore the ratio of the rates of formation of Na_3^+ and Na_2^+ ions is

$$\frac{\dot{N}_{\mathrm{Na}_3^+}}{\dot{N}_{\mathrm{Na}_2^+}} = \frac{\sigma_{\mathrm{MA}}}{\sigma_{\mathrm{AA}}} \frac{v_{\mathrm{MA}} n_{\mathrm{Na}_2}}{v_{\mathrm{AA}} n_{\mathrm{Na}}}\,.$$

The latter equation connects the atom-molecule AI cross-section and the corresponding atom-atom AI cross-section,

$$\sigma_{\mathrm{MA}} = \sigma_{\mathrm{AA}} \frac{\dot{N}_{\mathrm{Na}_3^+}}{\dot{N}_{\mathrm{Na}_2^+}} \frac{v_{\mathrm{AA}} n_{\mathrm{Na}}}{v_{\mathrm{MA}} n_{\mathrm{Na}_2}}\,,$$

since the ratio of the ion signals is measured, and the other parameters (particle densities and relative velocities) are known. Furthermore, we have assumed that the

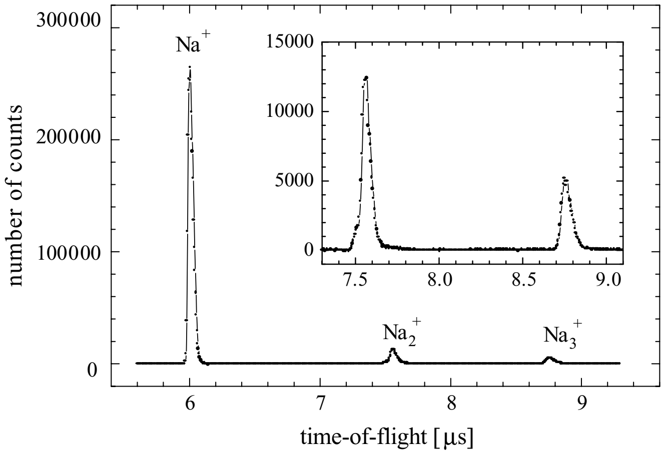

Fig. 4. Time-of-flight mass spectrum obtained when Na atoms are excited to the $4d_{5/2}$ state.

detection efficiency is the same for both the dimer and the trimer ions. We find for the cross-sections for AI in collisions of $Na_2(X^1\Sigma_g^+, v'' = 0)$ molecules with $Na(4d_{3/2})$ and $Na(4d_{5/2})$ atoms

$$\sigma_{\rm MA}(4d_{3/2}) = 7.2\sigma_{\rm AA}(4d_{3/2})$$

and

$$\sigma_{\rm MA}(4d_{5/2}) = 5.9\sigma_{\rm AA}(4d_{5/2})\,.$$

We have also applied the vibrational excitation to the Na_2 molecules. No noticeable change in the efficiency of trimer ion formation was observed when the molecules were vibrationally excited.

3.2 $Na_2(v'') + Na(5s)$ collisions

Formation of Na^+, Na_2^+, and Na_3^+ ions was also observed in collisions of Na_2 with $Na(5s_{1/2})$. The Na^+ ions are formed in a Penning process or by a photoionization, in analogy to the processes (10) and (11) [7,18]. The atom-atom AI process (6), involving atoms in their $5s$ and $3s$ states, is endothermic by 42 meV, which exceeds the mean atom-atom collision energy in our experiment (1.4 meV) by a factor of 30 and thus does not contribute to the formation of Na_2^+ ions.

The dependence of the Na_2^+ signal was nearly quadratic with respect to the power of laser 1 ($3s \rightarrow 3p$ excitation, see Fig. 2c), but linear with respect to the power of laser 2 ($3p \rightarrow 5s$ excitation, see Fig. 2d). This suggests that the Na_2^+ ions are formed in the AI process (8). Quadratic dependence on the power of laser 1 is expected for process (8) since laser 1 is not only involved in the population of the $3p$ level, but also in the population of the $5s$ level. The determination of the cross-section of the atom-molecule AI process (3) yielding Na_3^+ ions in collisions of $Na_2(X^1\Sigma_g^+, v'')$ and $Na(5s)$, following the procedure discussed in Section 3.1, is not possible since the absolute concentration of atoms in the $3p$ state is not known. Within the given signal-to-noise ratio no variation of the Na_3^+ signal was observed when the Na_2 molecules were excited to vibrational levels $v'' > 0$ using the FCP method.

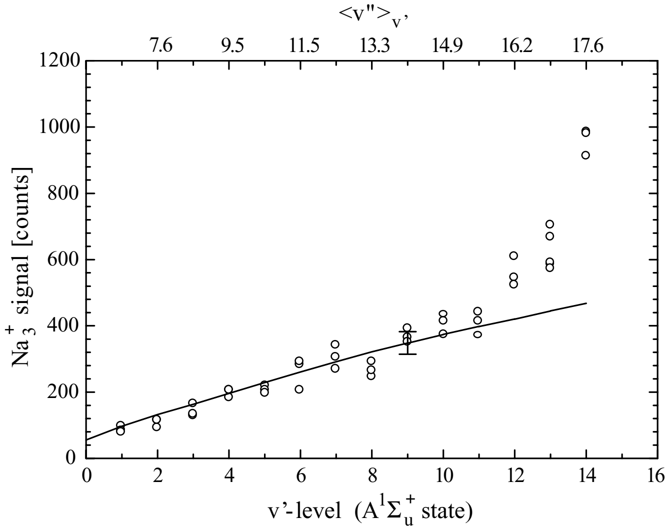

Fig. 5. Vibrational dependence of the rate of trimer ion formation by the process (14) using the Franck-Condon pumping method. The lower horizontal scale gives the vibrational level v', which is excited in the $A^1\Sigma_u^+$ state. Fluorescence from this level establishes a population distribution $f_{v'}(v'')$ over vibrational levels in the electronic ground state. The corresponding mean vibrational excitation $\langle v''\rangle_{v'}$ is given above the upper horizontal scale of the frame. The open circles give the experimental data. The solid line gives the expected vibrational level dependence, based on equation (15) and using the parameters obtained from the STIRAP data, shown in Figure 6 (see also eq. (16)). Good agreement is found up to levels $v' = 11$. For $v' = 14$, a fraction of 36% of the molecules in the initial state ($v'' = 0$, $J'' = 9$) is transferred to levels in the range $27 \leq v'' \leq 29$.

3.3 $Na_2(v'') + Na(3d)$ collisions

Only Na^+ and Na_2^+ ions were observed when the atoms were excited to the $3d_{5/2}$ level but the Na_2 molecules remained in their vibrational ground state. The formation of atomic ions are due to Penning and photoionization processes [18,19]:

$$Na(3p, 3d) + Na(3d) \rightarrow Na^+ + Na + e\,, \tag{12}$$

$$Na(3d) + h\nu \rightarrow Na^+ + e\,. \tag{13}$$

The Na_2^+ ions are formed in the AI process (9).

Ions from the atom-molecule AI reaction

$$Na_2(X^1\Sigma_g^+, v'') + Na(3d_{5/2}) \rightarrow Na_3^+ + e \tag{14}$$

were observed only with vibrationally excited Na_2 molecules. The variation of the Na_3^+ signal with vibrational excitation, while the density of $Na(3d_{5/2})$ atoms was kept constant, is given in Figure 5. Franck-Condon pumping establishes a vibrational distribution $f_{v'}(v'')$, which depends on the level v' excited in the $A^1\Sigma_u^+$ electronic state

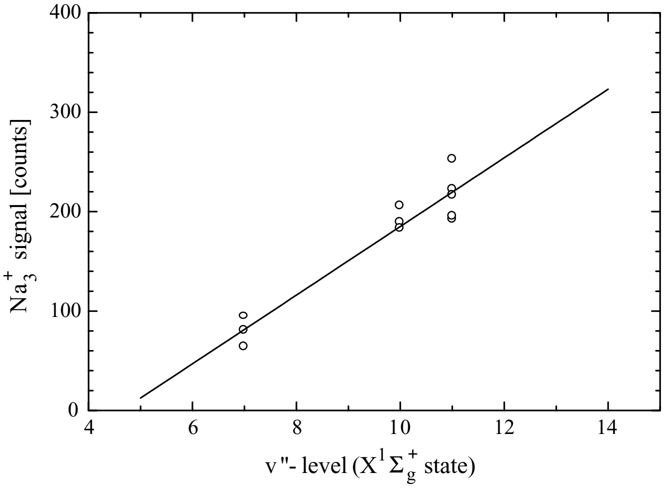

Fig. 6. Vibrational dependence of the Na_3^+ ion signal due to $Na_2(X^1\Sigma_g^+, v'')$ + $Na(3d_{5/2})$ collisions. The level v'' is selectively populated by the STIRAP method. Open circles are the experimental points, normalised to 100% population transfer efficiency. The solid line is a linear least-squares fit to the experimental data.

(see also Fig. 3). From $f_{v'}(v'')$ a mean value $\langle v''\rangle_{v'}$ of vibrational excitation can be determined. The ion yield increases smoothly with $\langle v''\rangle_{v'}$, with a marked increase of the slope found for $\langle v''\rangle_{v'} > 15$.

The rate of the trimer ion formation is determined by a convolution of the v''-dependent cross-section $\sigma(v'')$ for the process (14) with the population distribution $f_{v'}(v'')$ of the Na_2 molecules:

$$\dot{N}^{\mathrm{FCP}}_{\mathrm{Na}_3^+}(v') = \kappa \sum_{v''} \sigma(v'') f_{v'}(v''), \tag{15}$$

where κ is a constant factor relating the cross-section to the signal. The distribution function $f_{v'}(v'')$ is normalised such that $\sum_{v''} f_{v'}(v'') = 1$. The population of the optically pumped level of the molecules was always fully depleted during their interaction time with the pump laser, therefore the factor κ does not depend on v' or v''.

The attempts to model the vibrational dependence of the atom-molecule AI cross-section in (15) using a step function

$$\sigma(v'') = \begin{cases} 0, & v'' < v_{\mathrm{th}}, \\ \sigma_{\max}, & v'' \geq v_{\mathrm{th}}, \end{cases}$$

fail to reproduce the observed trimer ion signal v'-dependence. The experimental v'-dependence suggests a smooth increase of the cross-section with v'', the slope of which increases for high v''. The v''-dependence of the trimer ion signals, $\dot{N}^{\mathrm{STIRAP}}_{\mathrm{Na}_3^+}$, was also measured using the STIRAP technique for selective excitation of the levels $v'' = 7$, 10 and 11 (see Fig. 6). From the data of Figure 6 we find

$$\dot{N}^{\mathrm{STIRAP}}_{\mathrm{Na}_3^+}(v'') = \kappa\sigma(v''),$$

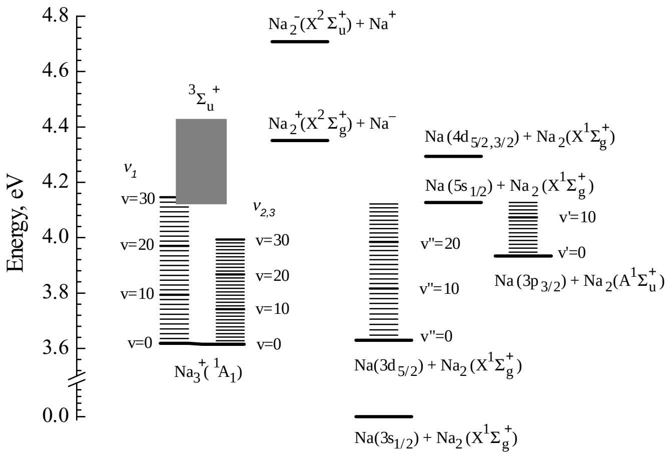

Fig. 7. Energy diagram for the Na_2 + Na system. Zero energy is chosen at the $Na(3s) + Na_2(X^1\Sigma_g^+)$ dissociation limit of the ground-state Na_3 molecule. The dissociation energy and ionisation potential of Na_3 are taken according to [20]. The levels v'' and v' correspond to the vibrational excitation energies in $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ states. The $Na(3p_{3/2})$+ $Na_2(A^1\Sigma_u^+, v')$ collision system with $11 \leq v' \leq 14$ has the same energy as $Na(3d_{5/2}) + Na_2(X^1\Sigma_g^+, v'')$ with $26 \leq v'' \leq 29$. Other relevant energies are given as well. The energy of the Na_3^+ $^3\Sigma_u^+$ state is not well known. The shaded area indicates the range of this energy, predicted by different studies.

with

$$\kappa\sigma(v'') = \begin{cases} 0, & v'' < 5, \\ -160 + 34.5v'', & v'' \geq 5. \end{cases} \tag{16}$$

The use of equation (16), with the parameters determined from the STIRAP data, in equation (15) nicely reproduces the results obtained by the FCP method up to $v' = 11$ or $\langle v''\rangle_{v'} = 15$ (see the solid line of Fig. 5). From the deviation of the data for $v' > 11$ from the line given by equation (16) we conclude that the cross-section increases significantly for $v'' \geq 26$ and the reasoning is as follows. The population by spontaneous emission is negligibly small for $v'' \geq 26$ when the excitation is via the level $v' = 11$. When excitation is via levels $12 \leq v' \leq 14$, significant population is established in vibrational levels in the range $26 \leq v'' \leq 29$. Judging from the deviation of the observed ion signal from the solid line (which is based on Eqs. (15) and (16)) for $v' > 11$, we conclude that the cross-section for trimer ion formation increases strongly for $v'' \geq 26$.

4 Discussion

This work deals with the dependence of the atom-molecule associative ionisation process yielding Na_3^+ ions in Na^* $+Na_2(X^1\Sigma_g^+, v'')$ collisions on the initial vibrational excitation of the molecules while the atoms are excited to the $3d$, $5s$ or $4d$ levels. The cross-sections for the AI process involving Na($4d$) atoms could also be determined by comparison with previously measured cross-sections for atom-atom associative ionisation [6] in collisions of Na ($4d$) and

Na (3*s*) atoms, yielding Na_2^+ ions. The cross-sections for atom-molecule AI was found to be 7.2 and 5.9 times larger, for atoms in the $4d_{3/2}$ and $4d_{5/2}$ level, respectively, as compared to the atom-atom AI process. The cross-section for the $Na(4d_{5/2}) + Na_2(X^1\Sigma_g^+, v'')$ is by about a factor of three larger than the one reported in [3]. In the case of the 5*s* state determination of the atom-molecule AI cross-section was not possible because the main contribution to the Na_2^+ signal is due to the $Na(3p) + Na(5s)$ collisions, and not due to the $Na(3s) + Na(5s)$, as it was supposed in [3].

The atom-molecule AI process with the atoms excited to the 5*s* or 4*d* level proceeds efficiently with molecules in their vibrational ground states, $v'' = 0$. Considering the fact that only 8% of the molecules are excited to higher-lying vibrational levels when either the Franck-Condon pumping technique or the STIRAP method is used, and for the given signal-to-noise ratio, we conclude that the cross-section for the atom-molecule AI process varies by less than a factor of two in the range $0 \leq v'' \leq 29$.

The formation of Na_3^+ ions in the atom-molecule AI process with atoms in the $3d_{5/2}$ level, process (14), was not observed for molecules in their vibrational ground state. In fact, the process is exothermic by only 13 meV (see Fig. 7) [20]. Additional energy seems to be needed to form Na_3^+ ions. Based on the vibrationally selective data, obtained by the STIRAP technique, the data obtained by the FCP method were nicely reproduced (see Fig. 5). From that result we conclude that trimer ion formation requires vibrational excitation to levels $v'' \geq 5$. This could be caused by a barrier in the Na_3 potential surfaces with respect to AI. The cross-section varies approximately linearly with v'' in the range $5 \leq v'' \leq 25$. The increasing density of states of the Na_3^+ ion with increasing energy may cause this vibrational level dependence. For $v'' \geq 26$ the cross-section rises much faster with v'' than for $v'' \leq 25$. Thus, the character of the vibrational level dependence changes at a total (electronic and vibrational) energy of $4.078 \leq E_{\text{tot}} \leq 4.122$ eV relative to the ground-state Na_3 dissociation limit to $Na_2 + Na$. It is interesting to note that a similar vibrational level dependence of the atom-molecule AI was observed in the process $Na(3p_{3/2}) + Na_2(A^1\Sigma_u^+, v') \rightarrow Na_3^+ + e$, the character of which changed also at a total energy (electronic and vibrational) of $4.087 \leq E_{\text{tot}} \leq 4.127$ eV [5]. We tentatively attribute these observations to the opening of a new electronic channel at the product side. In fact, a theoretical study [21] suggests that the excited ${}^3\Sigma_u^+$ state of Na_3^+, with the nuclei in linear configuration, lies approximately 0.66 eV above the bend electronic ground state at total energies of 4.28 eV. The marked enhancement in the trimer ion production efficiency at $v'' \geq 26$ may thus indicate that the energy of the ${}^3\Sigma_u^+$ is lower than predicted in [21]. However, more detailed information about the potential energy surfaces, and possibly new experiments which also determine the energy of the free electron after the AI process, are needed before final conclusions can be drawn.

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