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Vibrational effects in $Na_2(A\,^1\Sigma_u^+, v') + Na(3p_{3/2})$ associative ionization

A. Ekers [a,b,*], O. Kaufmann [a], K. Bergmann [a], J. Alnis [a,b], J. Klavins [b]

[a] *University of Kaiserslautern, Department of Physics, D-67653 Kaiserslautern, Germany*
[b] *University of Latvia, Institute of Atomic Physics and Spectroscopy, LV-1586 Riga, Latvia*

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Abstract

Associative ionizing $Na_2(A\,^1\Sigma_u^+, v') + Na(3p_{3/2})$ collisions have been studied in a single supersonic beam with respect to the influence of the initial vibrational excitation of the molecules on the reaction efficiency. An enhancement of trimer ion yield of nearly one order of magnitude has been observed as the vibrational excitation increases from $v' = 0$ to $v' = 14$.

From the large variety of atom–atom associative ionization (AI) processes, the best studied is the reaction of Na(3p) atoms,

$$Na(3p) + Na(3p) \to Na_2^+ + e, \tag{1}$$

the detailed studies of which have contributed significantly to the understanding of mechanisms of the AI processes (see for details Ref. [1] and references therein). Molecule–atom AI has been observed recently for three different situations: (i) in collisions of ground state atoms with highly excited molecules [2]; (ii) in collisions of highly excited atoms with ground state molecules [3]; (iii) in collisions of excited atoms with the molecules excited in their first electronically excited state [4]. In the latter work, the process

$$Na_2\left(A^1\Sigma_u^+\right) + Na\left(3p_{3/2}\right) \to Na_3^+ + e, \tag{2}$$

was studied in a vapour cell with excitation of only the lowest vibrational levels $v' = 0$ and 1 in the $A\,^1\Sigma_u^+$ state. The cross-section was found to be about one order of magnitude higher than that of the AI process (1). None of the studies [2–4] considered the influence of vibrational excitation of the molecules on the Na_3^+ yield.

It is well known that initial vibrational excitation affects the reactivity in atom–molecule exchange reactions [5]. The cross-section may increase [6] or decrease with increasing excitation. A dramatic increase with v'' has been observed in the process of dissociative attachment of low-energy electrons to the vibrationally excited molecules [7–9]. Recently vibrational effects have also been observed for the process of dissociative charge transfer in collisions

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[*] Corresponding author. E-mail: ekers@physik.uni-kl.de

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between sodium dimers and atoms proceeding through highly excited Na_3 potential surfaces [9]. There was evidence [10] that vibrational effects do play a role also in the case of molecule–atom AI. The complexity of such processes is, however, increased because of the additional degrees of freedom of the triatomic molecule which is formed.

The present study is performed using a single supersonic Na/Na_2 beam arrangement with time-of-flight (TOF) mass analysis to distinguish the trimer ions from Na_2^+ ions produced in the atomic AI process (1). Low intra-beam collision energies and concentration of the molecules in their lowest vibrational level provide favourable experimental conditions. They help to establish a relatively high density of molecules in the excited states by optical excitation. The beam expands from an oven operated at $T = 900$ K, through a 0.4 mm diameter nozzle, the temperature of which is held 50 K higher than the oven temperature. The divergence of the beam is reduced to about 1° by two skimmers, which results in a residual transverse Doppler width of 40 MHz. The density of the atoms and molecules in the reaction region 20 cm downstream from the nozzle are correspondingly $n_{Na} \approx 2 \times 10^{11}$ cm^{-3} and $n_{Na_2} \approx 2 \times 10^{10}$ cm^{-3}. Most of the Na_2 molecules in the beam (99%) are concentrated in the lowest vibrational level ($v'' = 0$) while about 1% are in $v'' = 1$. The population distribution over the rotational levels reaches its maximum for $J'' = 7$, as determined by laser-induced fluorescence measurements. The flow velocity of the particles in the beam, and the velocity distribution of atoms and molecules are readily measured by means of the Doppler shift technique [11,12]. The beam velocity is 1340 m/s and the mean relative velocity of molecules and atoms is 112 m/s, which corresponds to a mean collision energy of $\bar{E} \approx 1.6$ meV.

Two linearly polarised laser beams L_1 and L_2 (diameter 3 mm), with the direction of their linear polarisation adjusted parallel to the particle beam axis, were overlapped in the collision region (Fig. 1). The frequency of the first laser L_1 (a CR-699 cw single mode ring dye laser operated with Rh6G dye) was tuned to the $3s_{1/2} \rightarrow 3p_{3/2}$ ($F'' = 2 \rightarrow F' = 3$) transition. The laser L_1 beam was directed in the reaction region through a diaphragm to provide a homogeneous intensity profile. The loss of atoms to the $F'' = 1$ level of the ground state, which is not accessible for laser excitation, was small because the power of the laser L_1 was kept below the saturation limit, the typical intensity being 10 mW/cm^2. At higher laser intensities, power broadening leads to simultaneous excitation of the $F' = 2$ hyperfine component, from which spontaneous decay to the $F'' = 1$ is possible.

The second laser L_2 (a CR-699 cw ring dye laser, DCM dye) was used to excite the molecules from the ground $X\,^1\Sigma_g^+$ state to individual vibrational levels ($0 \leqslant v' \leqslant 14$) of the $A\,^1\Sigma_u^+$ state, using the R transi-

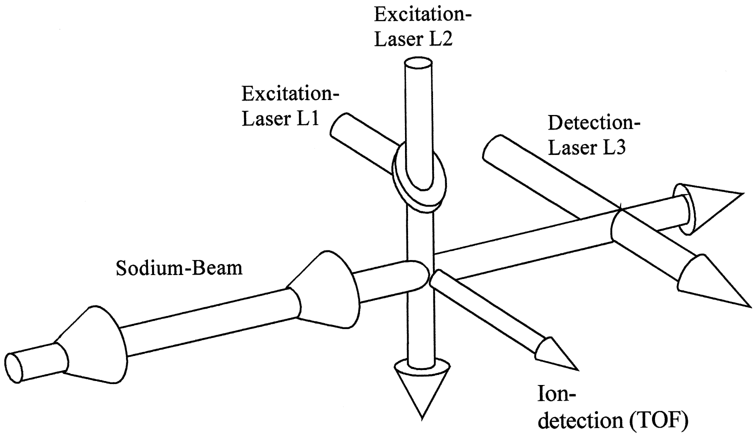

Fig. 1. Schematic arrangement of the experiment with the lasers for excitation of atoms (L_1) and molecules (L_2) as well as for monitoring (L_3).

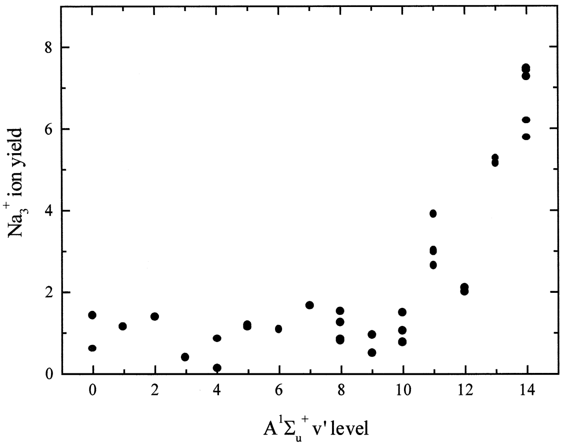

Fig. 2. Experimental dependence of the Na_3^+ ion yield on the vibrational quantum number v' of the $A\,^1\Sigma_u^+$ state.

tion $J''=9 \to J'=10$. A sharp edge cuts the upstream part of the L_1 and L_2 intensity profiles and prevents optical pumping of molecules upstream from the reaction region. A third laser L_3 (a CR-699 cw ring dye laser, DCM dye), which intersects the molecular beam 20 cm downstream from the reaction region, is used to verify the molecular excitation. Its frequency is tuned to $v''=0 \to v'=5$ R transition with $J''=9$. When the molecules are excited in the reaction region, optical pumping leads to a reduction of the L_3 induced fluorescence signal. This provides, in combination with the wavemeter readings, an unambiguous verification that the desired molecular transition is excited.

The power of laser L_2 was chosen high enough to saturate the molecular transition in order to ensure an excitation efficiency of unity for molecules in the level $v''=0$, $J''=9$ during the passage through the laser beam. This allowed us to disregard the different Franck–Condon factors (FCF) of the various $v''=0 \to v'$ transitions.

The production rate of trimer ions produced in the reaction volume V is given by

$$\frac{\mathrm{d}N_{\mathrm{Na}_3^+}}{\mathrm{d}t} = K_{\mathrm{MA}}^{\mathrm{AI}} \int_V [\mathrm{Na}^*][\mathrm{Na}_2^*]\,\mathrm{d}V, \tag{3}$$

where $K_{\mathrm{MA}}^{\mathrm{AI}}$ is the rate constant of the molecule–atom AI reaction (2), while $[\mathrm{Na}^*]$ and $[\mathrm{Na}_2^*]$ are the densities of excited atoms and molecules, respectively. Since there is only negligible optical pumping in the atomic excitation process, the density of excited atoms $[\mathrm{Na}^*]$ follows the laser L_1 spatially filtered intensity profile (weak excitation limit), which is assumed to be constant over the reaction volume. Provided that the molecular transitions are saturated and all the molecules of the lower $(v''J'')$ level are pumped, the integral $\int_V [\mathrm{Na}_2^*]\,\mathrm{d}V$ is independent on the FCF for the respective transition and does not depend on the laser power. Therefore, any variation of the Na_3^+ ion signal on v' measured at constant power of laser L_1 (3s–3p excitation) reflects the v' dependence of the rate constant $K_{\mathrm{MA}}^{\mathrm{AI}}$.

The experimentally observed dependence of the Na_3^+ ion yield on the vibrational quantum number v' is given in Fig. 2. All the data points are normalised to the same density of $Na(3p_{3/2})$, which is proportional to the square root of the simultaneously observed Na_2^+ signals resulting from process (1). This accounts for the slight variations in the flux of excited atoms due to frequency jitter of laser L_1. The rate constant of trimer ion formation is nearly independent of the vibrational excitation in the range $0 \leqslant v' \leqslant 10$. For $v' \geqslant 11$ it increases significantly with v'. For $v'=14$ the ion yield is about 7 times larger than for $v' \leqslant 10$. Several pairs of $v''=0 \to v'$

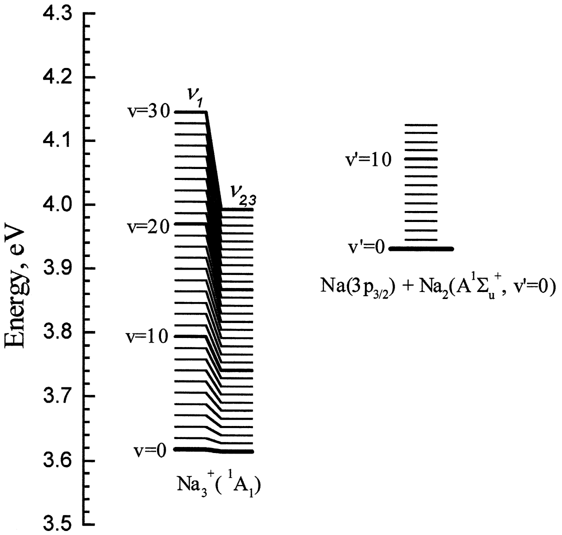

Fig. 3. Energy diagram for the $Na_2(A\,^1\Sigma_u^+) + Na(3p_{3/2})$ colliding system. Na_3^+ ground $^1A'_1$ state energy is given according to Ref. [13]. ν_1 and $\nu_{2,3}$ correspond to different Na_3^+ vibrational modes (anharmonicity is not accounted for).

transitions possess very similar FCF. For instance, for excitation of $v'=3$ and $v'=14$, or $v'=5$ and $v'=11$, the FCF are nearly the same. In that case, conclusions about the relative Na_3^+ yields do not rely on assumptions about the vibrational dependence of the integral in Eq. (3).

Even for $v'=0$ the reaction (2) is exoenergetic (Fig. 3). Reliable information on the potential surfaces for the $Na_2(A\,^1\Sigma_u^+) + Na(3p_{3/2})$ collision complex is not available at present. A quantitative interpretation of the results is therefore not possible. However, we mention two possible reasons for the observed vibrational dependence of the reaction rate constant. On one hand, the increase of the rate constant with v' could be related to a potential barrier in the entrance channel which is overcome by vibrational energy of the molecules. This would lead to a vibrational dependence of the formation of Na_3^+ ions in their ground $^1A'_1$ state of triangular configuration of the nuclei with a distinct onset at a specific vibrational energy. On the other hand, the vibrational dependence could result from the opening of a new exit channel which is energetically not accessible for molecules in their low vibrational levels. In particular, formation of a linear Na_3^+ molecule in $^3\Sigma_u^1$ (first excited) state is energetically possible at enhanced vibrational excitation of the Na_2 molecule. In fact, we find from the Na_3 ionisation potential according to Ref. [13] and relative positioning of the Na_3^+ states given in Ref. [14] that vibrational excitation to levels $v' \geqslant 14$ provides enough energy to open the channel leading to the formation of the Na_3^+ in the $^3\Sigma_u^+$ state. However, more precise computational results are needed to verify the latter statement.

We have observed vibrational effects also in AI of the ground state $Na_2(v'')$ molecules with Na(3d) atoms. It is interesting to note that a distinct increase of the rate of Na_3^+ formation is observed for those levels $v''=26-29$, which coincide energetically with the distinct change of the slope of the rate constant with increasing v' for the reaction (2) at $v'=11-14$. This seems to support the hypothesis about the formation of Na_3^+ in its $^3\Sigma_u^+$ state. Studies of the AI with Na(3d) atoms are in progress and will be reported elsewhere.

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