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Associative ionization in collisions between Na($3P_{3/2}$) and Cs($6P_{3/2}$)

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The results of an experiment on the associative ionization collision between sodium and cesium excited atoms are reported. The atoms are excited by two resonant cw lasers to the $3P_{3/2}$ and $6P_{3/2}$ levels, respectively, and the formation of the NaCs^+ molecular ion is observed. The rate constant of such process has been measured relative to the known rate constant of sodium associative ionization and its value resulted in $K=(5.4\pm3.2)\times10^{-11}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$.

I. INTRODUCTION

Collision processes between excited atoms give information on the interaction potentials of atoms and molecules, and they may be a powerful tool for spectroscopic analysis. Moreover, they are important to determine the evolution of a vapor under resonant laser excitation. These collisions can produce highly excited atoms, through the so-called energy-pooling collisions;[1] molecular ions, through associative ionization;[2,3] and atomic ions or atoms in autoionizing states, through energy-pooling ionization.[4] The combination and competition of these processes in very dense vapors can create large effects such as, for example, the formation of a plasma under relatively low-laser power-density excitation[5] or redistribute the populations of the different levels by creating, in some cases, population inversions and laser amplification.[6]

The alkali-metal atoms have been widely investigated and many energy-pooling and associative ionization cross sections have been measured. Despite their apparent simplicity, the analysis of these atoms presents many difficulties and much important information about them is still missing. Sodium is the best known and the cross section for the associative ionization

$$\mathrm{Na}(3p)+\mathrm{Na}(3p)\rightarrow\mathrm{Na}_2^+ + e^- \tag{1}$$

has been recently measured in optical confinement areas,[7] which has opened the new field of cold collision physics.

While cross section measurements are almost complete for homonuclear alkali-metal atom collisions, the same is not true for the heteronuclear ones. In this last case only cross-section measurements of energy-pooling collisions[8] and of Hornbeck-Molnar ionization collisions[9,10] are available. This last process is described by the reaction

$$A^{**}+B\rightarrow AB^{+}+e^{-}\ , \tag{2}$$

where A^{**} indicates a Rydberg atom.

This lack of data is not due to a weaker interest in heteronuclear processes, but to major difficulties to be overcome: alkali-metal atoms in vapor mixtures have quite different and not easily predictable vapor pressures; more than one resonant laser is needed and many different parameters have to be controlled and measured.

In order to study heteronuclear associative ionization, we built up an apparatus of crossed atomic beams that allows simultaneous detection and analysis of ion yields and fluoresence spectra. The experimental apparatus and the measurement procedure are described in the following as applied to the reaction:

$$\mathrm{Na}(3P_{3/2})+\mathrm{Cs}(6P_{3/2})\rightarrow\mathrm{NaCs}^{+}+e^{-}\ , \tag{3}$$

whose rate constant $K(\mathrm{NaCs}^+)$ has been measured relative to reaction (1).

II. EXPERIMENTAL APPARATUS

The apparatus, shown in Fig. 1, consists of two main parts: a vacuum chamber, where a turbomolecular pump keeps the background pressure to less than 10^{-8} Torr and where the atomic beams and the ion detection system are located; a double laser system for the atom excitation. The apparatus allows both ion detection and mass spectroscopy, with the help of a quadrupole mass filter, and fluorescence detection and spectrum analysis with the help of a monochromator.

The two atomic beam ovens are placed one in front of the other and are independently heated and controlled at ±1 °C. They cross in a collision cell where the ions are produced at a well-defined potential with respect to the mass analyzer. In the collision cell, as proved by the Doppler-broadened absorption linewidth, a vaporlike condition is obtained as a consequence of the atom-atom and atom-wall collisions. The ions are extracted by two electrostatic lenses, mass analyzed by a quadrupole filter, and detected by an electron multiplier. The ionic signal is then amplified and sent either to a multichannel analyzer or to a counter. A side hole in the collision cell permits collection of the emitted fluorescence which, by means of an optical fiber, is sent to a 1-m monochromator and analyzed.

A frequency stabilized ring dye laser is tuned to the sodium D_2 line, while a monomode diode laser (STC-model LT 50 A-03U), tuned also to the D_2 transition, is used to excite cesium atoms. The two laser beams, whose frequencies are controlled by reference cells, are superimposed with the help of a dichroic mirror and focused to an optical fiber. Light coming out from the other side of the fiber is focused into the collision cell. The typical spot diameter is 2 mm. By using suitable pinholes mounted on micrometer precision slides, we checked that the volumes excited by the two lasers in the collision cell differ by less than 5%. Maximum laser powers at the exit of the fiber are 10 mW at 852.1 nm and 100 mW at 589.0 nm; both intensities can be independently lowered by an optical neutral density filter.

A hot tungsten filament, placed near the collision cell, permits ionization of the vapors by allowing relative density measurements of the ground-state atoms.

III. MEASUREMENT PROCEDURE

The determination of the rate coefficient of a collision process between excited atoms requires the measurement of many parameters, such as the densities of the excited atoms, the effective lifetimes of the excited levels, the absolute calibration of the detecting apparatus, etc. Systematic errors can easily be made and carried to values which may differ by more than one order of magnitude.[11] A heteronuclear sample creates even more troubles, so an absolute measurement of rate coefficient of process (3) appears very complicated. A valid solution, even if obviously a little bit less precise, consists of a measurement relative to known cross sections which can be easily compared with the one of interest.

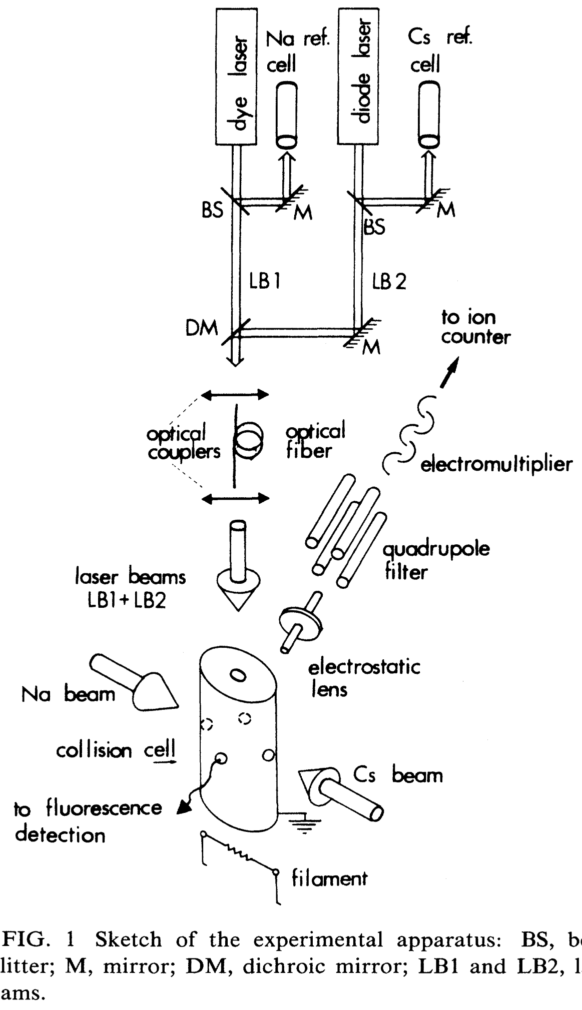

FIG. 1 Sketch of the experimental apparatus: BS, beam splitter; M, mirror; DM, dichroic mirror; LB1 and LB2, laser beams.

In our case, for example, the excitation of the two atomic species also produces the homonuclear ions through the reactions

$$\text{Na}(3P)+\text{Na}(3P)\rightarrow \text{Na}_2{}^{+}+e^{-}\ , \tag{4}$$

$$\text{Cs}(6P)+\text{Cs}(6P)\rightarrow \text{Cs}_2{}^{+}+e^{-}\ , \tag{5}$$

which can be detected together with NaCs^+ and whose associative ionization cross sections have been previously measured. But, while the rate coefficient $k(\text{Na}_2^+)$ has been measured several times, $K(\text{Cs}_2{}^+)$ has been measured only once and without great accuracy. The $k(\text{Na}_2{}^+)$ values converge to $K(\text{Na}_2{}^+)=(3.4\pm1.4)\times10^{-11}\ \text{cm}^3 s^{-1}$ reported in Ref. 12. This value, after the vaporlike condition in the collision region was verified, has been doubled according to the analysis made by Bezuglov *et al.*(13), which introduces a statistical factor for identical colliding particles under various experimental conditions. For the homonuclear cesium rate coefficient there exists only the not recent value $k(\text{Cs}_2{}^+)=2\times10^{-13}\ \text{cm}^3 s^{-1}$ that was obtained by using a resonance lamp and without ionic mass analysis.[14] This very low value can be justified by the fact that process (5) is highly endothermic; its energy defect is in fact $\Delta E=+2200\ \text{cm}^{-1}\cong 10kT$. We were unable to measure $K(\text{Cs}_2{}^+)$ because the $\text{Cs}_2{}^+$ ions were detectable only in the presence of very high cesium density, where it is difficult to have a correct evaluation of the experimental parameters. In these conditions systematic errors can be made due, for example, to radiation trapping, which may both modify the excitation volume and lead to a very erroneous evaluation of the excited atom density.

For these reasons, the following measurement procedure has been adopted in which $k(\text{NaCs}^+)$ is determined only relative to $K(\text{Na}_2{}^+)$. The $\text{Na}_2{}^+$ and NaCs^+ ionic yields are given by

$$I(\text{Na}_2{}^+)=k(\text{Na}_2{}^+)n^2(3p)e\epsilon(\text{Na}_2{}^+)(V/2)\ , \tag{6}$$

$$I(\text{NaCs}^+)=k(\text{NaCs}^+)n(3p)n(6p)e\epsilon(\text{NaCs}^+)V\ , \tag{7}$$

where $n(3P)$ and $n(6P)$ are the laser-excited populations of sodium and cesium, respectively; e is the electron charge; V is the interaction volume which is the same for sodium and cesium; and $\epsilon(m)$ is the efficiency of the apparatus for the ion mass m. The factor 2 in the denominator of Eq. (6) corresponds to the statistical factor discussed above. In our conditions $\epsilon(m)=\epsilon_0/\sqrt{m}$ is inversely proportional to the square root of the ion mass m.

Dividing Eq. (7) by Eq. (6), we get

$$K(\text{NaCs}^+)\cong 0.9K(\text{Na}_2{}^+)\frac{I(\text{NaCs}^+)}{I(\text{Na}_2{}^+)}\frac{n(3P)}{n(6P)}\ . \tag{8}$$

The measurement of the ratio between the excited densities of Na and Cs is then necessary. This can be done by detecting the emitted fluorescence and by remembering that

$$I_{nP} = h\nu_{nP}\zeta_{nP}\frac{n(nP)}{\tau_{nP}}\frac{\Delta\Omega}{4\pi}V \; , \tag{9}$$

where I_{nP} is the fluorescence intensity, ν_{nP} is the laser frequency, ζ_{nP} is the optical detection efficiency, $\Delta\Omega$ is the collection angle, and τ_{nP} is the effective lifetime of the excited level. It is then possible to derive the ratio between the excited atomic densities:

$$\frac{n(3P)}{n(6P)} = \frac{I_{3P}}{I_{6P}}\frac{\nu_{6P}}{\nu_{3P}}\frac{\zeta_{6P}}{\zeta_{3P}}\frac{\tau_{3P}}{\tau_{6P}} \; , \tag{10}$$

where the two lifetimes may be affected by radiation trapping. In this case, the effective lifetime can be expressed as $\tau = \alpha\tau_0$. τ_0 is the natural lifetime and α the radiation trapping coefficient. The values adopted in our calculations are $\tau_0(\mathrm{Na}) = 16.9$ ns and $\tau_0(\mathrm{Cs}) = 30.9$ ns.[15] In order to reduce the radiation trapping, the measurements have been performed at quite low densities, where this effect is negligible. The upper limit of the atomic densities in the collision cell is in fact lower than 10^{12} cm^{-3} as derived by the measured ratio between the D_1 and D_2 sodium lines, $I(D_1)/I(D_2) < 10^{-5}$, and by the rate coefficient for fine-structure exchange that is of the order of $K = 10^{-9}$ cm$^3 s^{-1}$. In any event, to give a quantitative evaluation of the relative weight of the radiation trapping effect, we considered its contribution by applying Milne's theory.[16] For a cylindrical geometry, close to our case, the lifetime increases by a factor $\alpha = 1 + (2\sigma nd/\mu)^2$, where σ is the optical cross section of the transition, n is the atomic density, d is the optical pathway, and μ is the solution of the equation $\mu\tan(\mu) = 2\sigma nd$.

The correction term for the lifetime ratio $\rho = \alpha(3P)/\alpha(6P)$ has been numerically solved and it is shown in Fig. 2 for different atomic density ratios $r = n(\mathrm{Na})/n(\mathrm{Cs})$. As one can see, ρ tends to 1 when $r = r_0 \cong 3.9$. In this case, radiation trapping affects both lifetimes in the same way and no correction must be introduced in Eq. (10).

r has been measured by ionizing the atoms with the electrons emitted by the hot tungsten filament and it has been fixed in order to be close to r_0. The electron impact ionization cross sections of Na and Cs have been taken from Ref. 17. Measurements have been also carried out by varying r around r_0, but no appreciable variations in the results have been observed, thereby confirming that our estimate for n is correct.

To summarize, $K(\mathrm{NaCs}^+)$ is obtained by measuring the relative intensities of the $\mathrm{Na_2}^+$ and NaCs^+ ion peaks, the fluorescence line intensities of the two fundamental transitions, and by correcting for the self-trapping by operating at $r = 3.9$.

IV. RESULTS

The ion spectra are obtained by scanning the mass transmitted by the quadrupole filter and by averaging the signal with the help of a multichannel analyzer. When the signals are extremely weak, an ion counting system coupled to a computer is used.

When the yellow laser is shined, only molecular $\mathrm{Na_2}^+$ ions are detected by confirming previous observations and by supporting the fact that associative ionization in sodium is a very effective process. When, on the contrary, only the diode laser is on, no ions are detected until very high cesium densities are reached. Then mainly atomic Cs ions are produced whose origin has to be ascribed to second-order processes. When both lasers are shined into the collision cell, ionic mass spectra such as the one showed in Fig. 3 are obtained. The more intense peaks correspond to $\mathrm{Na_2}^+$ and NaCs^+ masses, while secondary peaks occur at Cs^+ and Na^+ masses. The latter ones may be due to charge-transfer collisions with molecular ions that are efficient only at relatively high

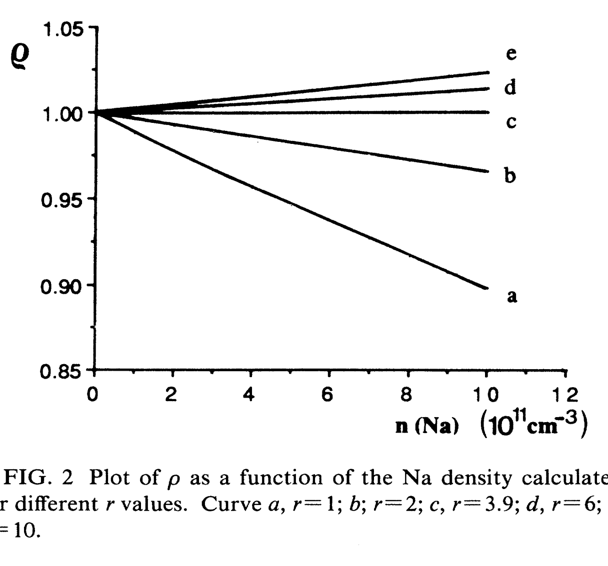

FIG. 2 Plot of ρ as a function of the Na density calculated for different r values. Curve a, $r = 1$; b; $r = 2$; c, $r = 3.9$; d, $r = 6$; e, $r = 10$.

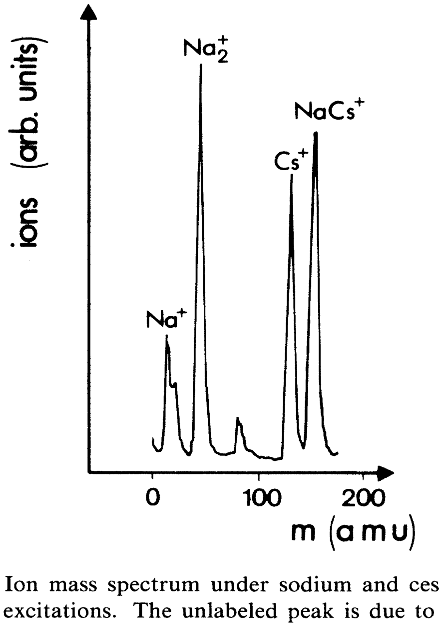

FIG. 3 Ion mass spectrum under sodium and cesium resonant laser excitations. The unlabeled peak is due to rubidium impurities.

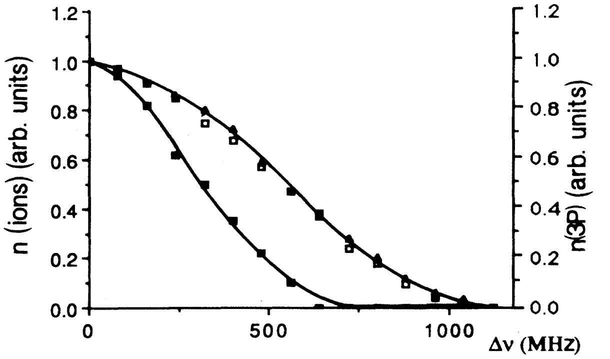

FIG. 4 Ion and fluorescence signals as a function of the yellow laser detuning. ■, $Na_2{}^+$; ▲, $NaCs^+$; □, D_2 sodium fluorescence. The curves represent an interpolation of the experimental data.

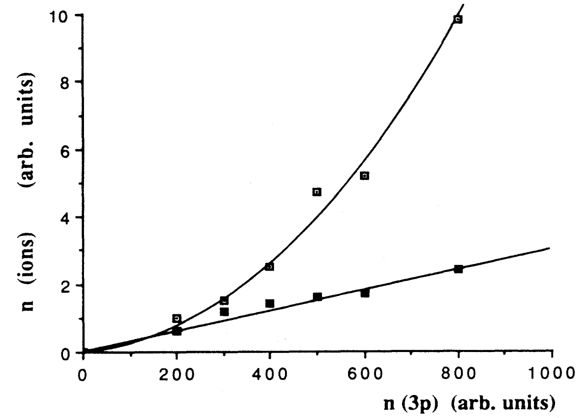

FIG. 5 $Na_2{}^+$ (□) and $NaCs^+$ (■) as a function of the sodium excited density. The curves are the quadratic and linear best fits of the experimental data.

ionic kinetic energy. In fact these peaks almost disappear when the extraction voltage is lowered. Another possible origin of the atomic ions may be found in energy-pooling collisions between excited sodium and cesium atoms which may populate almost resonantly many Rydberg cesium levels.[18] These atoms immediately ionize by collision or blackbody radiation. It is important to notice that when the sample is ionized by the electrons emitted by the filament, no trace of molecules is detected. The electron energy was set to 50 eV in order to match the experimental conditions, reported in Ref. 17, for the electron ionization collision cross-section measurements.

A further check that the molecular ion production is due to the associative ionization process has been obtained by fixing the mass of the quadrupole filter and by scanning the dye laser frequency around the resonance sodium line. The corresponding data, taken from the experimental curves, are reported in Fig. 4 where they have been normalized to make the comparison immediate. The fluorescence signal is also reported in the figure: as expected, the $Na_2{}^+$ and $NaCs^+$ signals go to zero out of resonance. The width of the $NaCs^+$ signal curve is equal to that of the D_2 fluorescence and it disappears when the diode is shut off, while the width of the $Na_2{}^+$ curve is about the half of the $NaCs^+$ one, as the quadratic dependence on $n(3P)$ requires. More precisely, the ratio between the two widths is about 1.6 instead of $\sqrt{2}$. This discrepancy may be due to a partial saturation effect of the sodium fluorescence which would modify the dependence of ion production. A more careful test was not possible in that way because, by reducing the laser intensity, the signal-to-noise ratio was not good enough. A more accurate check has been done by tuning the laser frequency to the center of the line and by varying its intensity by neutral density filters. Figure 5 shows a plot of the $Na_2{}^+$ and $NaCs^+$ signals as a function of the D_2 fluorescence. In this case they are very well fitted by a quadratic curve and by a linear curve, respectively.

By averaging over many ionic and fluorescence measurements and by using Eqs. (8) and (10), the rate-constant value

$$k(NaCs^+)=(5.4\pm3.2)\times10^{-11}\ cm^3 s^{-1}$$

has been obtained. The 60% indetermination is mainly due to the 40% factor of the reference rate coefficient $k(Na_2{}^+)$. By estimating the mean kinetic energy from Doppler width measurements, we get a mean collision velocity $\langle v\rangle=7\times10^4$ cm s^{-1}, then a cross section of the order of $\sigma(NaCs^+)=K(NaCs^+)/\langle v\rangle=8$ Å^2.

TABLE I. Heteronuclear alkali-metal molecular ion dissociation energies D_e and energy defects involved in associative ionization.

		D_e(cm^{-1})				ΔE_2 (cm^{-1})[b]			
Ion	ΔE_1 (cm^{-1})[a]	Ref. 19	Ref. 21	Ref. 20	Ref. 23	Ref. 19	Ref.21	Ref.20	Ref.23
NaK^+	4990	6450	3386	4612	4677	−1480	+1600	+378	+313
$NaRb^+$	3901	5402	2500	3967	3709	−1500	+1400	−66	+192
$NaCs^+$	2701	4596	1693	3209		−1895	+1008	−508	
KRb^+	7832	7015	4193	5750	5644	+816	+3639	+2082	+2188
KCs^+	6632	5967	2903	4596		+665	+3729	+2036	
$RbCs^+$	6858	5645	3145	4879		+1213	+3713	+1979	

[a] $\Delta E_1=V_{low}-[E(A^*)+E(B^*)]$, where V_{low} is the ionization potential.
[b] $\Delta E_2=\Delta E_1-D_e$.

V. DISCUSSION

The efficiency of an excited-state collision is connected with the energy defect of the process.[8] For instance, we have seen how the homonuclear associative ionization of cesium has a large energy defect and, consequently, a low rate coefficient. In the heteronuclear associative ionization collision between A and B atoms, the energy defect ΔE is determined by the difference between the final-state energy $E(AB^+)$ and the initial-state energy $E(A^*)+E(B^*)$. A limit for $E(AB^+)$ is given by the difference between the lowest ionization potential of the two atoms IP_{low} and the dissociation energy D_e of the molecular ion AB^+. The energy of the vibrational produced state should be subtracted to this value. In Table I the D_e and ΔE for heteronuclear alkali-metal molecular ions, as derived from theoretical works, are shown. The three calculated values of the NaCs^+ dissociation energy do not agree by a non-negligible quantity. The values calculated in Refs. 19 and 20 would imply that process (3) is esothermic, while Ref. 21 would imply an endothermic process. The value of the rate coefficient $k(\mathrm{NaCs}^+)$ that we have experimentally determined would confirm that process (3) is probably esothermic. In any case it is interesting to remark that the only available experimental value of dissociation energy of an heteronuclear alkali-metal molecular ion, the NaK^+,[22] is in agreement with Ref. 20. Also the values calculated in Ref. 23 for three different molecular ions are in agreement with Ref. 20.

The performed measurement offers the possibility of a check of the application of interatomic potential calculations to heavy atoms and at the same time gives a useful parameter for the diagnostics of laser-produced plasma and dense laser excited vapors.

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