

Photo associative reactions of laser cooled sodium

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We describe the novel technique of dynamical spectroscopy of transient molecules. We apply this technique to the study of ultra-cold collisions of Na atoms at 200 μK . By careful choice of laser intensities and detunings we can unravel the dynamics of these collisions and obtain information on interactions taking place at internuclear distances of 100–1000 a_0 and interaction energies below 1 μeV .

1 Dynamical spectroscopy of transient molecules

Due to the breakthrough of laser cooling techniques during the last 10 years it is nowadays possible to produce samples of cold atoms with sufficient density to study collisional processes. This has led to the exploration of a new field of (ultra-)cold collisions. Especially the study of cold collisions in the presence of a light field has been very successful. Three aspects have played a major role in this success, which are all due to the small relative velocity between the colliding atoms:

1. It is possible to excite two atoms in a free-bound transition to singly-excited states of the transient molecule formed in the collision, yielding a wealth of experimental information on the long-range interactions in these short-lived molecular states.
2. These molecular transitions show very small Doppler broadening, which makes it possible to resolve vibrational and even rotational structure of the states. The intensity of the different states provide detailed information on the dynamics of the interacting particles.
3. The number of partial waves contributing to the cross section is relatively low, which further reduces the complexity of the molecular spectrum.

We will refer to this new way of performing spectroscopy on colliding atoms as “dynamical spectroscopy of transient molecules”. This new field lies on the borderline between “traditional” fields in atomic and molecular physics, namely the fields of atomic collision physics, molecular spectroscopy and atom-light interactions. The language used in this field is therefore a mixture of the language used in these other fields and might in some cases be confusing.

In this contribution we will emphasize, that this new kind of spectroscopy can provide information of the dynamical aspects of the reactions and that it is

possible to obtain information on the path the reactions proceed. Dynamical spectroscopy is thus a way of probing these transient molecules, which have interatomic distances of several hundreds of a_0 and interaction energies far below μeV 's. In another contribution to this conference, P. Julienne describes, how laser cooled atoms can be used to obtain high-resolution spectroscopy on molecular states at long-range distances. From these experiments one obtains very detailed information, not only on the molecular aspects, but also on the atomic lifetimes of the states involved. We will not discuss this issue, but refer to the contribution of P. Julienne and a review article ¹.

2 Experimental setup

The experimental setup is depicted schematically in figure 1. We produce a cloud of Na atoms in a magneto-optical trap (MOT). The atoms in the MOT are cooled and trapped by the combined action of six, intersecting laser beams and an inhomogeneous magnetic field. The MOT is situated in a vapor cell. The laser beams capture atoms from the low-velocity tail of the Maxwell-Boltzmann distribution of the sodium vapor, since the capture velocity of the MOT is small compared to the average velocity of the atoms in the cell. The number of atoms in the MOT is 4×10^6 in a volume of 0.1 mm^3 , leading to a density of $4 \times 10^{10} \text{ atoms/cm}^3$. The temperature of the atoms is in the order of $200 \mu\text{K}$, which has been measured by observing the expansion of the atom cloud when the lasers are shut off. Atoms in the MOT collide with each other with a characteristic collision energy of 200 neV , orders of magnitude lower than collision energies at room temperature.

The MOT cloud is crossed with a probe laser. By focusing the probe laser we obtain a high atomic saturation parameter, however, since the probe frequency is detuned from atomic resonance the molecular transitions are not saturated. The molecular ions produced by the atomic interactions, that are initiated by the probe laser, are extracted and counted with a channeltron. The number of ions as a function of the detuning can then be measured. To verify that the probe laser does not destroy our MOT, we monitor its behavior by observing the fluorescence from the MOT with a photo diode.

The process of laser cooling and probing is continuously cycled with a frequency of 10 kHz . In order to achieve this we cool and trap the atoms for a period of $50 \mu\text{s}$, after which we block the cooling laser. Then we switch on the probe laser and detect the ions produced in this period of $50 \mu\text{s}$. This period is short enough to ensure that the atom cloud does not spread appreciably. This way we are confident that the ions are only produced by the probe laser, and not by the cooling laser.

Figure 1: Schematic representation of the setup.

3 Long-range predissociation in two-color photo association of ultra-cold Na atoms

In the case of sodium excitation of both sodium atoms provides sufficient energy to the transient Na_2 -molecule to reach the ionization continuum of Na_2^+ at short internuclear distance (see figure 2). This makes the ionization reaction exothermic and therefore allowed even at cold temperatures. One-color photoionization, where a single color is used for both excitation steps, yields information on the singly-excited states, since the second excitation does not contribute any structure to the ionization spectrum. One-color experiments, however, have the disadvantage that the intensity and frequency of the first and second excitation step cannot be changed independently leading to restrictions on the possible excitation schemes.

Therefore we have set out to perform a two-color photoionization experiment for ultra-cold Na atoms in a vapor-cell MOT ². The second frequency was generated as a sideband on the principal frequency by making use of the stimulated Brillouin scattering (SBS) process in a saturated fiber. Light scattered back in the fiber due to the saturation obtains a Stokes shift, which is proportional to the sound velocity of the phonons in the fiber. For our fiber (York HB600) this leads to a Stokes shift of $\Delta\omega_{SBS} \approx 28$ GHz, which allows us to generate two frequencies with a fixed frequency difference.

The nature of the second excitation step in the photoionization process in

Figure 2: Two-color photoionization for ultra-cold Na atoms. The processes PAAI and PAPI are discussed in the text.

the one-color experiments was rather unclear. Either the transient molecule could be ionized at short internuclear distance by direct photoionization, or the molecule would at large internuclear distance first be excited to a doubly-excited state, which crosses the ionic continuum at short internuclear distance (see figure 2). The first process is referred to as photo-associative photoionization (PAPI), whereas the second process is photo-associative autoionization (PAAI). In a two-color experiment the PAPI-process contributes to the spectrum as long as the frequency of the light is below resonance. However, the PAAI-process only contributes to the ionization spectrum below resonance in a window with a width $\Delta\omega_{SBS}/2$ due to the fixed relation between the two frequencies generated in the SBS process. In the experiment we only observed an ionization signal in this window showing that the ionization process is autoionization (PAAI).

Using two colors, for which one can independently control the intensity, we were able to obtain high-resolution spectra of the singly-excited 0_g^- -state of the Na_2 -molecule (see Fig. 3). This state is a long-range molecular state, since the inner turning point is at $55a_0$ and the state is totally determined by atomic parameters. The state has 43 bound vibrational levels, of which we were able to observe states with vibrational quantum number $v=8-19$. For the lowest states ($v=9,10$) we were able to resolve the rotational structure and we could determine rotational constants for these states. At the frequency where we expect a signal from the $v=20$ vibrational state the ionization signal becomes zero and for higher frequencies we observed an ionization signal, however, no well-resolved peaks were detected. From the calculated potential curves of the 0_g^- -state including hyperfine interaction we could ascribe the absence of the $v=20$ state to predissociation of the transient molecule due to hyperfine coupling at $350a_0$. The 0_g^- -state is coupled asymptotically with the

Figure 3: Dynamical spectroscopy of the transient Na₂-molecule. Note, the cutoff of the ionization near the predissociation limit.

Na(3P_{3/2})-Na(3S_{1/2}[*F*=2]) asymptote. However, out of 10 hyperfine states, which constitute the 0_{*g*}⁻-state, 8 are coupled to the Na(3P_{3/2})-Na(3S_{1/2}[*F*=1]) asymptote due to an avoided crossing at 350*a*₀. This crossing is located at the position of the *v*=20 state, which therefore predissociates before it can be formed. Higher lying states can be excited, however, due to the finite velocity at the avoided crossing there is a finite probability that these states also predissociate leading to a lifetime broadening of the peaks. No well-resolved peaks are therefore observed.

4 Vibrational state distribution of Na₂⁺-ions created in ultracold collisions

The PAAI and PAPI process both produce a Na₂⁺-ion and an electron. To make a further distinction between the two processes we have set out an experiment to detect the vibrational state distribution of the Na₂⁺-ion³. This vibrational state distribution depends on the way the ions are created. In the PAPI process the ions are formed by direct photoionization and the population of the different vibrational states depend on the Franck-Condon overlap between the singly-excited state and the ionic states. In the PAAI process

Figure 4: Measured dissociation spectrum of Na_2^+ -ions formed in cold collisions of Na atoms.

the ionic states are populated by a curve crossing of the doubly-excited state with the ionic continuum, and therefore the vibrational distribution depends strongly on position of this curve crossing with respect to the position of the vibrational states. From theoretical calculation this crossing is predicted around the $v=3$ vibrational state.

The experimental set-up is as follows. The molecular ions produced in the vapor-cell MOT are extracted with a set of electric plates to a region, where they are photo dissociated by ≈ 100 mW of laser light, which is strongly focused to obtain a appreciable dissociation ratio of $\approx 0.1\%$. The laser excites the molecule to a strongly repulsive state, which leads to the dissociation of the molecule. The frequency of the dissociating laser is scanned and the dissociation rate is measured as a function of the frequency. Since the upper state is strongly repulsive transitions occur for given frequency at well-defined internuclear distance of the molecule. The measured ionization rate therefore closely resembles the probability distribution of the ionic state to a large extent.

The measured spectrum (see Fig. 4) clearly shows four peaks, which is a strong indication that most of the ions are formed in the $v=3$ vibrational state. However, from the non-zero minima in between the peaks we can infer that also other vibrational states are formed. By fitting the measured spectrum

with a calculated spectrum, in which the calculated dissociation spectrum of the different vibrational states are used as input and the vibrational state populations are fit parameters, we obtain a good agreement between theory and experiment. Of all allowed states only the $v=2$ and 3 are populated (29% and 71%, respectively). This result is another indication that the PAAI process is the dominant ionization mechanism in cold collisions. For the PAPI process a broad distribution of all energetically accessible vibrational states of Na_2^+ would be expected.

5 Conclusions

Dynamical spectroscopy of transient molecules is a new way of performing spectroscopy on molecular states, which can not be probed otherwise. Typical interatomic distances probed by the laser light are in the order of $100\text{--}1000a_0$ and typical interaction energies are well below $1\ \mu\text{eV}$. By using a careful choose of laser frequencies and intensities we are able to unravel the excitation mechanism in case of two colliding Na atoms at a collision energy of 20 neV. We show that the auto-ionization process is clearly favored over the photo-ionization process, once the first process becomes energetically allowed. Furthermore, we have shown that it is possible to detect the vibrational distribution of the molecular ions, which are formed in the cold collisions. This distribution is sharply peaked around the $v=3$ vibrational states, which is another indication that the auto-ionization process is favored.

In the near future we will also include metastable helium in our studies. In our view helium has with respect to alkali-systems several advantages. We mention the relatively simple electronic structure, which makes detailed comparisons with theory possible, and the process of Penning ionization of the He_2 -molecule, which can be studied in great detail. Penning ionization of the He_2^* -molecule is a special case of 3-body dynamics.

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