VELOCITY DISTRIBUTION AND DIMER FORMATION IN A Na/Na$_2$ BEAM

K. Bergmann, U. Hefter, P. Hering
Fachbereich Physik der Universität Kaiserslautern

Using the TOF via optical pumping method[1,2] and the Dopplershifted laser induced emission[3] described in the preceding paper, we measured the parallel and perpendicular velocity distribution respectively for Na atoms and Na$_2$ molecules in a variety of individual quantum states. In addition we monitored the flux of molecules in specific states while changing the stagnation pressure. In all cases we found a significant dependence on the internal energy of the molecules. The goal of these experiments is to improve our understanding of the beam dynamics and the dimer formation process.

Two TOF spectra for molecules in different levels are shown in Fig. 1. A difference in flow velocity $u_{\parallel}$ and temperature $T_{\parallel}$ can be seen. Fig. 2 shows the variation of $u_{\parallel}$ with the oven temperature for molecules in different quantum states and for the atoms. Over the whole temperature range $u_{\parallel}$ is larger than expected from isentropic expansion. The most remarkable feature is the reversal of the ordering of the flow velocity versus internal energy between the low and high temperature regime. This behaviour can be traced back to the dimer formation process. The observation of the intensity variation of molecules in particular quantum states provides more detailed information about the dimerisation (see Fig. 3). A simple model calculation for the population and depopulation of a specific level during the expansion shows that the non monotonic variation is caused by the competition of different contributions to the population. At low temperature the intensity increases because of the rising oven pressure, at an intermediate temperature relaxation into lower lying states depletes the population while at high temperature the dimer formation via atomic recombination is the dominant process. A more detailed analysis indicates, that originally the molecules are not formed in low lying states, but levels of intermediate energy are populated in the primary process.

The redistribution of the heat of formation plays a key role in the beam dynamics. The number density at T = 850 K is about 10 times less the density at 1020 K. On the low temperature side the density is not high enough for a complete redistribution of

the excess energy. The molecules formed in the beam will retain some additional kinetic energy. After the formation, on their way into the free molecular flow region, they will still suffer many elastic collision causing an effective deceleration. Simultaneously, the internal energy of the molecules will be removed via inelastic collisions resulting in a small gain in kinetic energy. Nevertheless, since the molecules undergo many more elastic collisions the net effect is a deceleration. Molecules found in $v = 0$ are not formed in the beam with a large relative rate but are brought into that state via collisions. Consequently they will have suffered more collisions than molecules escaping into the free molecular flow region with more internal energy. Their deceleration to the average flow velocity is nearly complete and they will be slower than molecules in higher states.

At high temperature, i.e. density, the molecules undergo several thousand collisions and the excess energy is completely absorbed by the bulk system. The mechanism responsible for the ordering of the flow velocity vs internal energy at low temperature is no longer dominant. Most of the molecules will relax into low lying states (cooling of internal degrees of freedom). The population of the vibrational levels, however, cannot be described by a single vibrational temperature. We found increasing excess population for levels of increasing energy. Again molecules found downstream with high internal energy represent a group of particles that has suffered fewer collisions compared to those with most of their internal energy removed by collisions. Thus we expect the most complete acceleration and cooling of $T_\parallel$ for molecules in $v = 0$.

The velocity slip observed between the atoms and the molecules follows naturally from the picture outlined above. The heat of formation contributes to the acceleration of the beam, i.e. the m o l e c u l e s are the driving species accelerating the atoms. Thus we expect a slightly lower velocity for the atoms.

References

1) T.D. Gaily, S.D. Rosner, R.A. Holt, Rev. Sci. Instruments, $\underline{47}$, 143, 1976

2) K. Bergmann, U. Hefter, P. Hering, J.Chem.Phys. ,$\underline{65}$, 488 1976

3) K. Bergmann, W. Demtröder, P. Hering, Appl. Phys.$\underline{8}$, 65, 1975

4) A similar curve for the (3/43) level has been observed by A.G. Visser et al. Chem. Phys. (to be published)
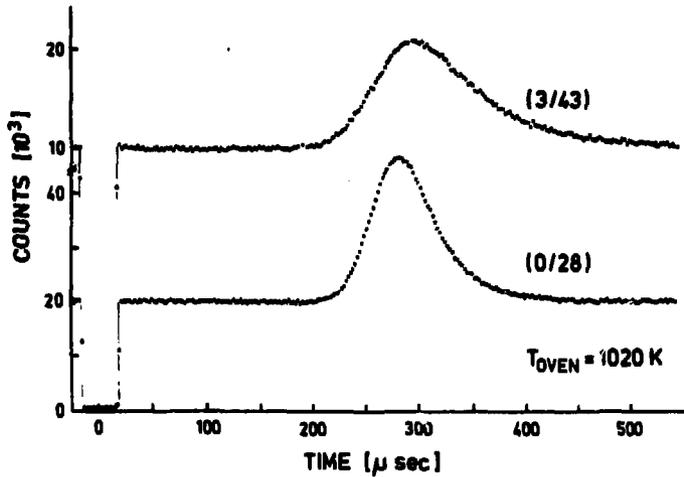
Fig. 1: TOF spectrum via optical pumping for molecules in two (v,J) states. The flow velocity as well as the width of the distribution is significantly different.
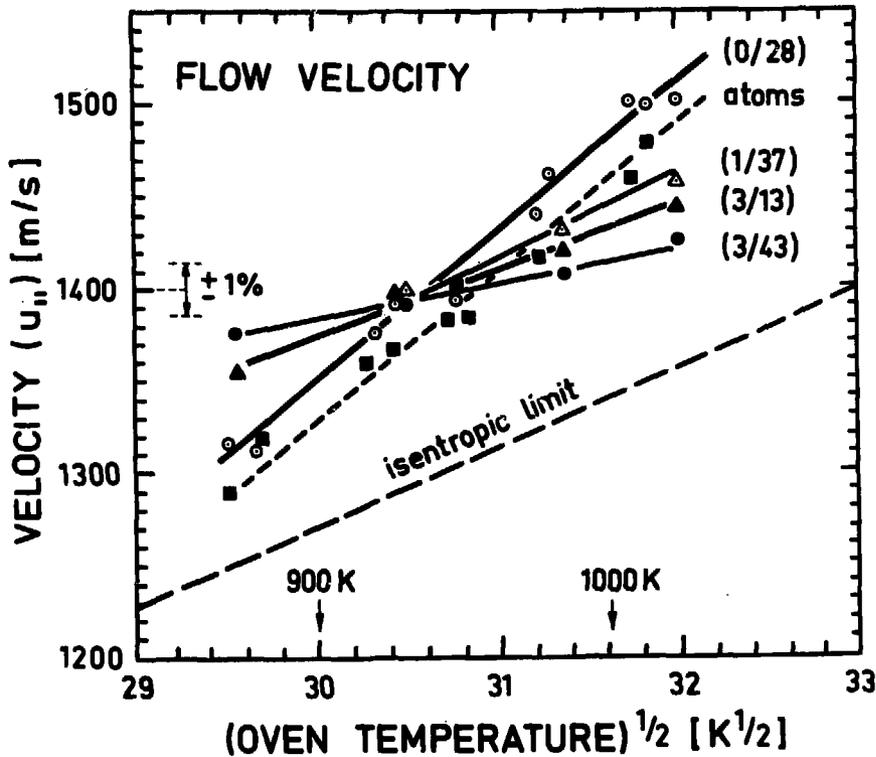

Fig. 2: Flow velocity $u_{||}$ of Na atoms and Na$_2$ molecules in different (v,J) states in a supersonic beam. Nozzle diameter was 0.2 mm. The nozzle temperature was kept 70 to 100 K above the oven temperature. The isentropic limit is calculated for an ideal monoatomic gas and based on the oven temperature since we found no variation of $u_{||}$ when changing the nozzle temperature by 60 K.
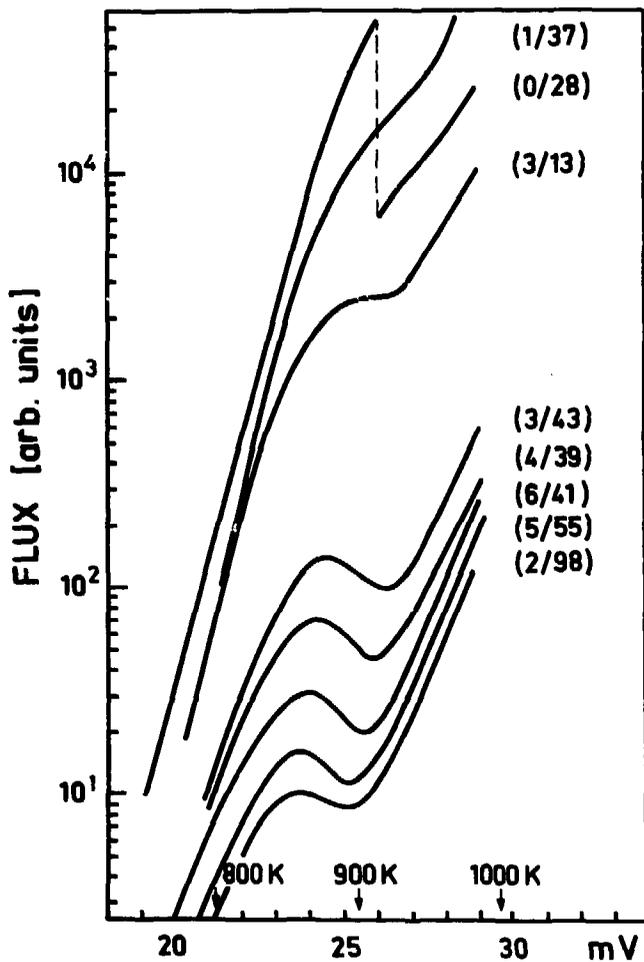
Fig. 3: Variation
of the flux of mo-
lecules in a par-
ticular state (v,J)
with oven tempera-
ture. The ordering
of the curves is
based on internal
energy (e.g.
$(2/98)$: 1800 cm^{-1}
$(5/55)$: 1300 cm^{-1}
$(0/28)$: 200 cm^{-1})
The steep rise in
the high tempera-
ture side is due
to formation of
molecules in the
beam. It shifts to
higher temperature
with increasing
energy. The slope
is proportional to
the cube of the
number density in
the oven.