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Geminate recombination processes induced by rare gas collisions with predissociating NaI molecules prepared by femtosecond excitation*

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Abstract. NaI molecules predissociate after excitation with ultrashort pulses at a peak wavelength of 320 nm. In rare gas environments at higher pressures the process of geminate recombination is likely to occur. We studied the dynamics of these processes under various pressure conditions and for different collision partners. The calculations were performed within a three-dimensional statistical model which simulates the NaI wave-packet dynamics with classical trajectories and the collisions via an instantaneous hard-sphere scattering.

Key words: Femtosecond spectroscopy – Collisions – Recombination

1 Introduction

In recent experiments the predissociation of NaI in rare gas environments was investigated under high-pressure conditions with the help of time-resolved femtoscond spectroscopy [1]. It was found that the oscillating transient signals which reflect the gas-phase predissociation dynamics [2–4] are destroyed with increasing pressure. Furthermore, it could be shown that the dissociation yield decreases with increasing pressure. This stabilization effect is due to energy relaxation in the NaI molecule, which reduces the Landau-Zener probability for transition into the exit channel. The NaI experiments are in the line of other femtosecond studies investigating high-pressure effects in I_2-rare gas collisions [5–7]. In the latter studies, clear evidence for caging of I_2, i.e. recombination through collisions, was found. Also, it could be shown by Zewail and co-workers [8] that the iodine molecule is able to recombine after short-pulse excitation above its B-state dissociation limit and single collisions with Ar atoms [9].

From a theoretical point of view the above-mentioned processes are difficult to simulate. A correct treatment would include a proper description of the femtosecond pump-and-probe transitions in the observed molecules and of the interaction of these systems with the environment. A very promising approach is to approximate the molecular wave-packet dynamics with swarms of classical trajectories and account for the collisions via a molecular dynamics calculation [10–15]. In previous work on the NaI-rare gas system we chose a similar but simpler approach [16, 17]. The wave packets were represented by a sample of classical trajectories but the collisions were treated as instantaneous and were assumed to occur with the hard-sphere scattering cross-section. This model could explain the trends observed in the experiments [16]. However, possible geminate recombination processes of NaI were ignored in our studies. The objective of the present paper is to remove this shortcoming and to investigate to which extent these effects play a role and possibly could be detected in a time-resolved femtosecond experiment. The paper is organized as follows: Sect. 2 summarizes the theoretical model. The results are given in Sect. 3 and Sect. 4 contains a summary and outlook.

2 Theory and model

The predissociation process of the NaI molecule was extensively investigated with the help of femtosecond pump/probe spectroscopy in the gas phase [2–4]. Figure 1 shows the relevant excitation scheme: femtosecond excitation from the electronic ground state $|0\rangle$ results in the preparation of a wave packet in the excited state $|1\rangle$. The potential curves of these states are of alike symmetry and show an avoided crossing around 7 Å. The non-adiabatic coupling induces a bifurcation of the packet each time it reaches the crossing region: the splitting results in a fraction which remains bound and a fraction which enters the asymptotic region. Thus we find a quasi-bound vibrational motion which is damped due to probability flux into the exit channel.

Here we set up a simple three-dimensional model where geminate recombination occurs if free Na and I atoms approach each other closer than the region of the crossing point (see Fig. 1). This

* Contribution celebrating the 60$^{\text{th}}$ birthday of Prof. Dr. Wilfried Meyer

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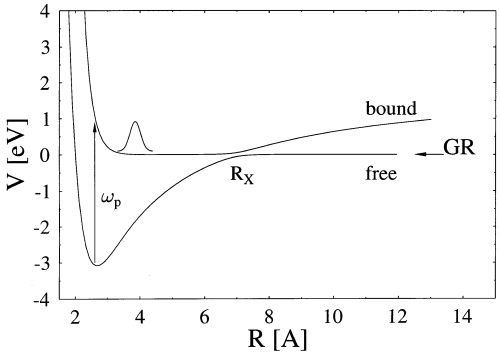

Fig. 1. Schematic illustration of the femtosecond excitation and recombination processes. Adiabatic potential curves for two electronic states of NaI which show an avoided crossing are displayed. The *vertical arrow* illustrates the excitation with a frequency ω_p which results in the preparation of a wave packet. The predissociation process can be reversed through geminate recombination (*GR*) induced by collisions

model yields relative recombination rates and in more detail we use the following description:

1. Trajectories describing free Na and I are started at the distance of the crossing point R_X with a fixed kinetic energy. The kinetic energy is taken from the energy distribution of the pump-pulse which prepares the excited state wave packet. The center-of-mass motion of NaI is taken into account by sampling from a Maxwell-Boltzmann distribution at a given temperature. The initial rotational motion of NaI is ignored.

2. The spatial distribution of the rare-gas atoms is assumed to be isotropic and the velocities are assumed to obey a Maxwell-Boltzmann distribution for a temperature of 960 K [1].

3. At each timestep Δt we choose at random the velocities of the rare gas atoms according to the Maxwell-Boltzmann statistics and calculate the collision probability P. The latter depends on Δt, the relative velocity $\mathbf{v}_{\mathrm{rel}}$ of the collision partners, the cross section σ, and the density ρ of the rare gas atoms. The density of NaI is assumed to be negligible [1]. Thus we have

$$P = \rho\sigma|\mathbf{v}_{\mathrm{rel}}|\Delta t \tag{1}$$

The cross sections were taken to be $\sigma = \pi(r_a + r_b)^2$, were r_a, r_b are atomic radii of the collision partners, i.e. we assume hard sphere scattering. The values of r_a, r_b were taken from Lennard-Jones distances [18] and the density is related to the pressure via the ideal gas equation. Care was taken to ensure that the probability is smaller than 1 even for large velocities $|\mathbf{v}_{\mathrm{rel}}|$ by choosing the time-step Δt small choose enough.

4. We choose a random number s from the unit interval and if $s < P$ a collision occurs. The collision leaves the center-of-mass velocity of the collision partners unchanged as well as the magnitude of their relative velocity. The orientation of the relative velocity after the collision is chosen at random. Since an isotropic distribution of the rare gas atoms is assumed, this amounts to an average over all impact parameters [19].

5. The calculation is stopped if Na and I are found at a distance smaller than the crossing point.

6. If recombination occurs, we calculate the Landau-Zener probability for surface hopping between the adiabatic electronic states [20]. A random number s_h is chosen from the unit interval and if $s_h < P_{LZ}$ we find the system in the excited electronic state $|1\rangle$. We note that because of the small relative velocity of the recombining atoms P_{LZ} is close to zero so that most trajectories remain in the ground electronic state.

From the above description it should be clear that the model simply consists of the integration of the classical equations for the relative motion of NaI and various Monte Carlo samplings. It is thus very easy to implement and computationally very efficient.

3 Results

Within the model described in the last section we may calculate the relative recombination ratio

$$G_r(t) = \frac{n(t)}{N_r} \tag{2}$$

where $n(t)$, is the number of trajectories for which the Na-I distance becomes smaller than the crossing point R_X at time t and N_r is the total number of trajectories. Figure 2 displays this time-dependent function for Ar-NaI collisions at different pressures. As can be expected, we find the recombination to be more effective at higher pressures. The curves increase with time yielding asymptotic values which, even for the 2000 bar case, do not exceed 40%.

A change of the collision partner, going from He to Xe, increases the probability for recombination. This is documented in Fig. 3 which contains $G_r(t)$ at a pressure of 1000 bar. Kinematic considerations show that, compared to Ar for example, a large number of collisions are necessary for recombination in the He case. This is more clearly demonstrated in Fig. 4. The upper panel (a) shows the recombination ratio at a time of 2 ps as a function of the number of collisions N_c. This quantity is defined as

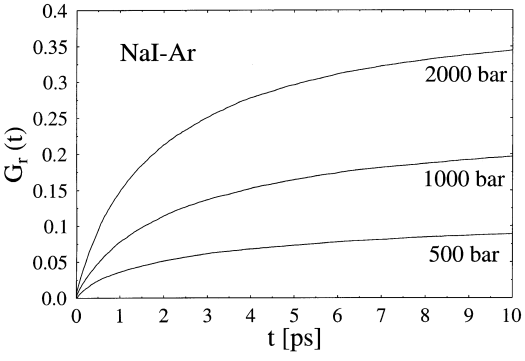

Fig. 2. Time-dependence of the relative recombination yield of free Na and I atoms induced by Ar collisions. Curves are displayed for

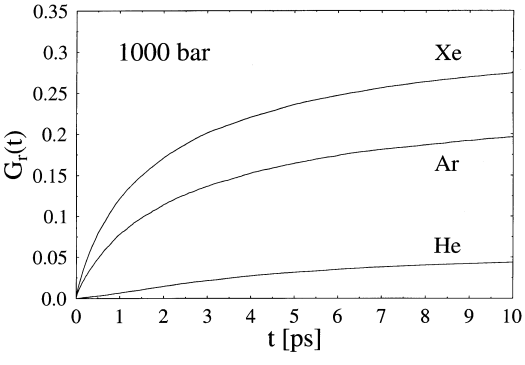

Fig. 3. Recombination yield of NaI molecules obtained from collisions with different rare gas atoms at a pressure of 1000 bar

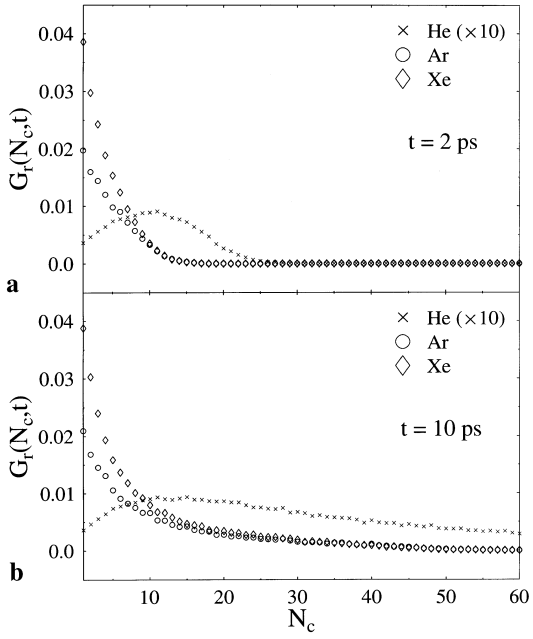

Fig. 4a, b. Relative recombination ratio $G_r(N_c, t)$ as a function of the number of collisions and for fixed times t. Results are displayed for He (multiplied with a factor of 5), Ar, and Xe and for times $t = 2$ ps (**a**) and $t = 10$ ps (**b**)

$$G_r(N_c, t) = \frac{n(t, N_c)}{N_r} \tag{3}$$

where $n(t, N_c)$ is the number of trajectories leading to recombination if N_c collisions occur. The first information we can take from the figure is that for Ar and Xe most recombination processes result from single collisions. This explains the fast increase of $G_r(t)$ for Ar and Xe as seen in Figs. 2 and 3. A different situation is encountered in the case of He, where recombinations are most probable for N_c between 5 and 15. Recombination induced by He-Na or He-I single collisions require He atoms which move very fast. This is only a small fraction under the present conditions and a strong dependence on temperature is to be expected. For longer times, multiple collisions become more probable, as can be seen in Fig. 4b which shows results obtained after a time of 10 ps. Again, for the heavier rare-gas atoms the single collisions yield most of the recombination yield. For He, multiple collisions over a wide range of N_c (10–30) result in similar values of $G_r(N_c, t)$. It is clear that these multiple collisions are more probable for the faster He atoms. Note also that only a very small number of trajectories recombine in the He case. Therefore our signals, which were obtained with 2×10^6 trajectories, show a remaining statistical noise.

Until now the model is not able to predict total recombination yields. To estimate these we use a classical description of the wave-packet dynamics in the quasi-bound molecule. This approximation was applied to the NaI-rare gas problem before [16, 17]. Briefly we use a set of classical trajectories $R_n(t)$ which are chosen to represent the quantum mechanical probability distribution. A Gaussian envelope function is assumed for the pump-pulse so that its spectral width defines a Gaussian energy distribution peaked at the energy corresponding to the laser frequency ω_p. According to the time and frequency distribution of the pulse we sample at random times t_n and energies ϵ_n and start trajectories at times t_n with zero momentum at the inner classical turning point where $V_1 = \epsilon_n$. Within this method the classical counterpart of the quantum mechanical wave packet prepared by the pump pulse in state $|1\rangle$ is

$$\rho_1^{cl}(R, t) = \frac{1}{N_{tot}} \sum_{n=1}^{N_{tot}} R_n(t) \tag{4}$$

where $R_n(t)$ are the trajectories with the initial conditions as specified above and N_{tot} is the total number of trajectories. If the trajectories reach the crossing region we calculate the Landau-Zener probability for the hopping process and proceed as described above to estimate on which electronic state the time-evolution is continued. The trajectories which leave the crossing region on the lower state are chosen as an input for our model of the recombination process (see above). In this way we are able to calculate the total recombination yield

$$G_{tot}(t) = \frac{n(t)}{N_{tot}} \tag{5}$$

where $n(t)$ is the number of trajectories which represent recombination.

Figure 5 shows $G_{tot}(t)$ for NaI-Ar collisions. Only a small recombination yield is predicted in the time-interval regarded here. Since the adiabatic coupling between the electronic states is weak, one finds only about 40% dissociation probability after 5 ps for zero pressure. However, at a pressure of about 500 bar the dissociation yield is just 15% at this time. This is due to the effective energy relaxation of the NaI molecules in the excited electronic state which reduced the dissociation probability. Regarding this number, it is understandable that only about 1% of the total number of trajectories correspond to recombination processes. This number is still an upper limit since our calculations stop in the moment a recombination occurs. The trajectories which reach distances smaller than the crossing point may still vanish

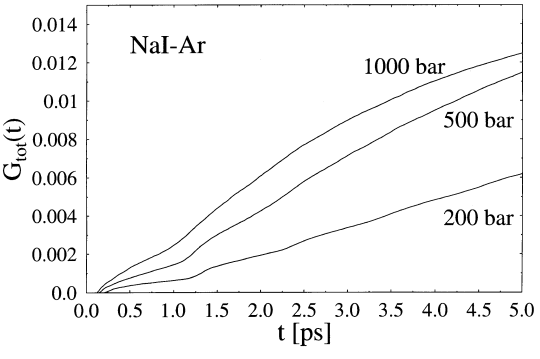

Fig. 5. Total recombination yield as a function of time and for the NaI-Ar system at different pressures

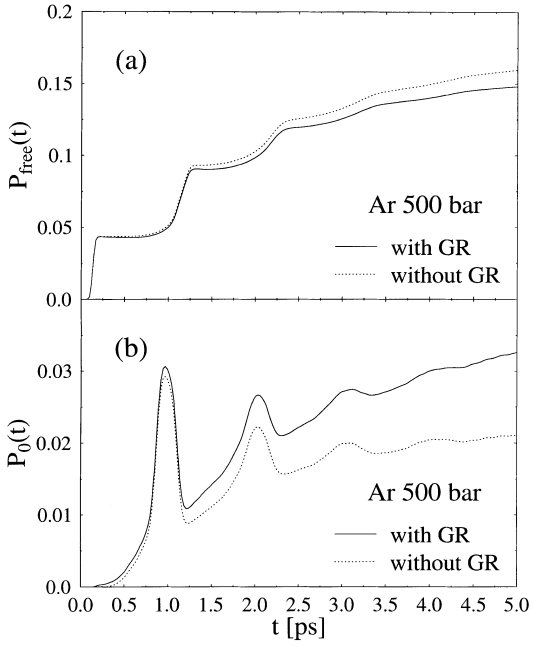

Fig. 6. a fraction of dissociated NaI molecules; curves from calculations including and neglecting GR processes are compared to each other as a function of time. **b** Fraction of bound molecules in the electronic ground state calculated with and without GR processes

in the asymptotic region at a later time. This is, however, not very probable since following collisions result in a vibrational relaxation in the ground state so that the orbits become bound.

The small yields do not change significantly if higher pressures or heavier collision partners are used. Concerning a pump/probe experiment under high pressure conditions, we conclude that the process of geminate recombination is very unlikely to be detected. This is demonstrated in Fig. 6, which compares calculations including and neglecting recombination processes. Figure 6a shows the total amount of dissociated molecules $P_{\text{free}}(t)$ for a pressure of 500 bar. The curve was obtained by counting the number of free trajectories in state $|1\rangle$ as a function of time. The characteristic step function, which is also found experimentally in case when the probe-pulse wavelength is chosen to detect free sodium atoms [2–4], reflects the quasi-bound motion of the molecule and the stepwise increase of the fragment population. There are only minor deviations in the two curves. The lower panel (Fig. 6b) displays the amount of bound molecules within the electronic ground state ($P_0(t)$). Here only those molecules which were excited in the pump process and return to the ground state are taken into account. Again, the temporal structure stems from the wave-packet motion and the separation of the peaks reflect the period of the vibrational motion. Although the two curves obtained with and without geminate recombination differ for longer times, the deviation is not dramatic so that the effect of recombination does not introduce a significant change of the basic temporal behavior.

4 Summary

We have investigated geminate recombination processes in the NaI predissociation process taking place in rare gas environments. The fragmentation is initiated by femtosecond excitation of NaI and recombination occurs via momentum transfer from He, Ar, or Xe to the Na and I atoms during collisions. A simple hard-sphere three-dimensional model is used to calculate recombination rates via Monte Carlo sampling. The efficiency of recombination is increased with increasing pressure and mass of the collision partner. However, the total recombination yield is found to be in the order of 1% of the number of dissociated molecules. An increase in pressure to much higher values will not result in a more efficient recombination, since at high pressures the NaI molecules become stable through energy relaxation which reduces the fragmentation probability.

In conclusion we predict that geminate recombination processes for the NaI-rare gas system occur only with small probability. As a consequence, femtosecond pump/probe signals will most likely not yield information about these processes.

The computational scheme we used here is very efficient and easy to implement. We have recently applied this model to the experiments of Wan et al. [8] on the caging dynamics of I_2 and found excellent agreement with experiment and also with quite involved quantum calculations [9]. This confirms our expectation that reliable results can be obtained using the model presented here.

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References

1. Knopp G, Schmitt M, Materny A, Kiefer W (1997) J Phys Chem A 101:4852
2. Rose TS, Rosker MJ, Zewail AH (1988) J Chem Phys 88:6672
3. Rosker MJ, Rose TS, Zewail AH (1988) Chem Phys Lett 146:175
4. Rose TS, Rosker MJ, Zewail AH (1989) J Chem Phys 91:7415
5. Lienau C, Zewail AH (1996) J Phys Chem 100:18629
6. Materny A, Lienau C, Zewail AH (1996) J Phys Chem 100:18650
7. Liu Q, Wan C, Zewail AH (1996) J Phys Chem 100:18666
8. Wan C, Gupta M, Baskin JS, Kim ZH, Zewail AH (1997) Chem Phys Lett 106:4353
9. Meier C, Engel V, Beswick A (1988) J Chem Phys Lett 287:487
10. Benjamin, J, Wilson KR, (1991) J Phys Chem 95:3514
11. Whitnell RM, Wilson KR, Yan Y, Zewail AH (1994) J Mol Liq 61:153
12. Li Z, Zadoyan R, Apkarian VA, Martens CC (1995) J Phys Chem 99:7453
13. Sterling M, Zadoyan R, Apkarian VA (1996) J Chem Phys 104:6497
14. Zadoyan R, Sterling M, Ovchinnikov M, Apkarian VA (1997) J Chem Phys 107:8446
15. Batista VS, Coker DF (1997) J Chem Phys 106:6923

16. Dietz H, Knopp G, Materny A, Engel V (1997) Chem Phys Lett 275:519
17. Dietz H, Engel V J Phys Chem A (in press)
18. Wilson JW, Heinbockel JH, Outlaw RA (1988) J Chem Phys 89:929
19. Woods LC (1993) An introduction to the kinetic theory of gases and magnetoplasmas. Oxford University Press, New York
20. Levine RD, Bernstein RB (1987) Molecular reaction dynamics. Oxford University Press, New York