CARS spectroscopy of the NaH₂ collision complex: the nature of the Na(3²P)H₂ exciplex – ab initio calculations and experimental results

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Abstract. CARS (Coherent Anti-Stokes Raman Scattering) has been used to analyze the rovibronic state distribution of H₂ after collision with Na(3²P). New lines, which do not correspond to H₂ lines are observed in the CARS spectrum. The experiments point to the formation of a complex of Na(3²P)H₂ in A²B₂ symmetry. Ab initio calculations of the A²B₂ potential were performed. On this surface the vibrational spectra of the exciplex are evaluated. The observed lines can be attributed to vibrational transitions in the complex, in which combinational modes are involved. The connection of experimental and theoretical results indicates that a collisionally stabilized exciplex molecule is formed during the quenching process.

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I. Introduction

The interpretation of experimental results on the quenching process of Na* (or Na(3²P)) by diatomics [1, 2] showed that knowledge of the relevant potential energy surfaces is an essential requirement for the understanding of this process. The assumption that features of the potential surfaces determine this process gave rise to several theoretical investigations [3–13]. The review article by Campbell et al. [2] gives a summary of the recent experimental and theoretical work on this subject. The most accurate computation of the quenching process with H₂ was carried out by Botschwina et al. [3]. From their results it was evident that only detailed ab initio calculations will lead to a thorough understanding of the involved potential surfaces and hence of the nature of the collision dynamics. One of their results was that the quenching process occurs most favorably for the C2v configuration, i.e., for the perpendicular approach as shown in Fig. 1. In the C2v configuration the crossing between the repulsive electronic ground state X²A₁ of NaH₂ and the weakly bound first excited state A²B₂ occurs at minimal energy, as illustrated in Fig. 2. Its energetic location can be reached under thermal conditions and thus the energy transfer process becomes possible for bulb experiments.

Even for the restricted C₂v symmetry not yet all questions of interest are solved quantitatively. The character...
of the bond between Na and H₂ in the $A^2B_2$ state is still controversial. According to Truhlar et al. [12] a crossing ionic state leads to the bond, while Botschwina et al. [3] concluded from their calculations that only a partial charge transfer over large regions of space occurs. It also was still unclear whether the potential well of the $A^2B_2$ state is deep enough to allow for the existence of bound vibrational states. The population distribution of the vibrational and rotational states of H₂ after collision is still not quantitatively verified by scattering calculations.

We have applied CARS (Coherent Anti-Stokes Raman Scattering) [14] as an experimental technique to measure directly the internal state distribution of H₂ after the quenching process in collision with Na($3^2P$) [15, 16]. With this method which we applied for the first time it is possible to measure the vibrational and rotational population in absolute quantity as well as the time dependence of the population and depopulation process. It is desirable to compare these experimental results with ab initio calculations.

In addition, new experimental data give evidence that we have formed a Na($3^2P$)-H₂ collision complex which was stabilized by an additional collision forming a stable Na($3^2P$)H₂ exciplex molecule. We were able to find CARS lines of this exciplex. To interpret our new experimental results, in particular the vibrational structure of the CARS spectra calculations to analyze the spectra are essential. In order to understand the involved collisional dynamics we needed highly accurate potential energy surfaces and a detailed vibrational analysis of the $A^2B_2$ state. The original data of Botschwina et al. [17] were not available to us. Therefore we decided to perform new calculations tailored to the questions of our interest. The present paper concentrates mainly on the $A^2B_2$ state of the NaH₂ complex.

II. Experimental section

Experimental setup

The experimental setup (Fig. 3) is similar to the one used in [16]. In a stainless steel heat pipe oven of 400 mm length and 22 mm diameter a gas mixture of Na and H₂ is provided. The laser beams are focused into the middle of the cell and recollimated back to parallel beams for detection. The sample cell can be heated to temperatures between 550–650 K corresponding to a sodium vapor pressure of approx. 10 μbar to 250 μbar. The H₂ pressure can be varied between 1 mbar up to 1000 mbar.

Scanning CARS laser system

The CARS pump laser and the CARS Stokes laser are dye lasers which are optically pumped by the same excimer laser at 308 nm with approx. 500 mJ pulse energy. The excimer laser output is split into two parts giving 30–40 mJ output energy of the CARS pump laser and 10–20 mJ for the Stokes laser both with a bandwidth of approx. 0.2 cm⁻¹ and a pulsewidth of approx. 10 ns. The pump laser wavelength was fixed in most experiments to 447 nm but can be varied. The Stokes laser is tunable and was scanned between 500 to 550 nm depending on the vibrational levels of H₂.

A flashlamp pumped dye laser (FPD-laser) with 1.5 μs pulsewidth is used to pump the sodium $3^2S \rightarrow 3^2P$ transition which is saturated. During the pulsewidth of 1.5 μs collisions of H₂ with excited sodium are possible and will lead to vibrationally excited H₂ which are then detected integrally with the CARS laser system. This time is defined as integration time.

Fig. 3. Experimental setup of the CARS experiment