

Comment

The collisional energy transfer between the $D^1\Pi$ and $d^3\Pi$ states of the NaK dimer induced by argon buffer gas

H. Zhiwei et al.: Appl. Phys. B 66, 471 (1998)

T. Hansson

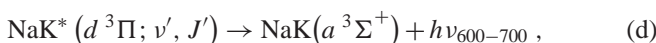
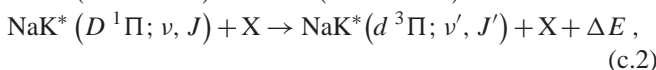
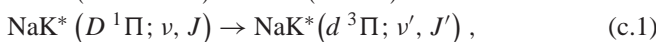
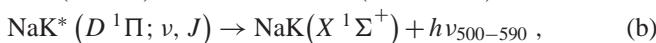
Department of Physics, Section of Atomic and Molecular Physics, Royal Institute of Technology, KTH, SE-100 44 Stockholm, Sweden
Department of Chemistry, Royal Institute of Technology, KTH, SE-100 44 Stockholm, Sweden

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Abstract. It is shown in this Comment that the method proposed by Zhiwei et al. to extract cross sections for collisional energy transfer between molecular states mediated by argon atoms, is neither correct nor suitable, as it fails to reproduce the molecular behaviour they observe. An alternative model based on a consecutive scheme is put forward, and it is shown that a minimal assumption of one intermediate collisionally activated step is enough to satisfactorily reproduce the observations by Zhiwei et al. However, the extracted parameters are functions of the involved rate constants that are too complex to leave any hope of attaining information on the desired cross sections from them by just varying the argon buffer gas pressure, as done by Zhiwei et al.

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Zhiwei et al. report in [1] on experimental cross sections for the collisional energy transfer between the $D^1\Pi$ and $d^3\Pi$ states in NaK induced by argon atoms. The measurements are performed in a heat-pipe oven, by monitoring the ratio of fluorescence intensity for certain $D^1\Pi(v, J) \rightarrow X^1\Sigma^+$ transitions to the intensity at a specific wavelength in the region of the $d^3\Pi \rightarrow a^3\Sigma^+$ transition as a function of argon pressure. The result is shown by the circles in Fig. 1. The reaction scheme they assume to analyse the data is (slightly modified for clarity):



where X is any collision partner. For the purpose of calculating the pressure dependence of the desired fluorescence

intensity ratio, Zhiwei et al. set up the rate equation

$$\frac{dN_d}{dt} = N_D(t)C_{D-d} - N_d(t)(A_d + C_d), \quad (1)$$

in which N_d and N_D are the instantaneous populations of the d and D states, respectively. The probabilities for the collisional transfer from the D to the d state is denoted by C_{D-d} , and C_d is the probability for collisional quenching of the d state. The radiative depopulation of the d state is included as A_d . Making the so-called steady-state assumption, the following relation for the ratio R_{D-d} of the fluorescence intensities

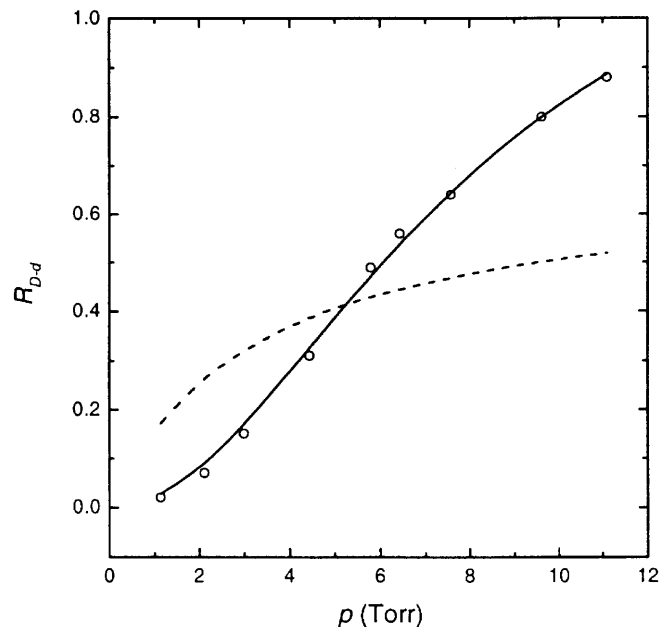


Fig. 1. Ar pressure dependence of the fluorescence ratio R_{D-d} . (O) data measured by Zhiwei et al. [1] as $I_{670\text{ nm}}/I_{534.4\text{ nm}}$; (---) curve obtained with the model in [1] and by including the collisional deactivation of the d state omitted there; (—) curve obtained by fitting (4) to the data points. Fit parameters: $a = 0.001$, $b = 0.001$, $c = 0.79$, $d = 18.34$, $e = 0.09$, $f = 0.30$, $\chi^2 = 0.0007$

$I_{\text{fl}}(D)$ and $I_{\text{fl}}(d)$ from the D and d states, respectively, is obtained:

$$R_{D-d} = \frac{I_{\text{fl}}(d)}{I_{\text{fl}}(D)} = \frac{C_{D-d}}{A_D + C_d A_D / A_d} = \frac{n\sigma_{D-d}\langle v \rangle}{A_D + C_d A_D / A_d}. \quad (2)$$

Here, A_D is the spontaneous emission rate for the D state, n is the density of collisional perturbers (assumed by Zhiwei et al. to consist only in Ar atoms), σ is the cross section for collisional $D \rightarrow d$ transfer, and $\langle v \rangle$ is the mean relative velocity. With the assumption that everything else is independent of pressure, Zhiwei et al. extract the cross section for collisional energy transfer by argon atoms from the seemingly linear part of the R_{D-d} dependence on argon pressure (Fig. 1).

The analysis outlined above is suffering from severe oversimplifications. Most important, the term $C_d = n\sigma_d\langle v \rangle$ introducing the probability for collisional quenching of the d state is assumed to be negligible when extracting σ_{D-d} . However, for the moment assuming we can neglect the contribution from all external perturbers except Ar, all the values going into (2) are measured in [1]. Putting these values into (2) and using the above relation for C_d the dashed line in Fig. 1 is obtained. Obviously, (2) is not able to reproduce the observed argon pressure dependence of R_{D-d} .

Furthermore, the assumption of neglecting the influence of collision partners other than Ar atoms, the most prominent being potassium atoms, is dubious. It is known [2], that the cross section for collisional quenching of the $D^1\Pi$ state by K atoms, $\sigma_{D,K}$, is large, about 1000 \AA^2 . This should be compared to $\sigma_{D,Ar}$ which is around 200 \AA^2 [1, 2]. At the temperature used in the experiment in Fig. 1, 621 K, the pressure of the K vapour is in the order of 1 Torr. This implies that at least the rate for quenching of the various involved molecular states will be significantly affected by the K atoms over the whole Ar pressure range in the experiment, 1 to 11 Torr, and that this has to be taken into account in setting up the rate equations governing the kinetics. Consequently, the radiative lifetime for the D state stated by Zhiwei et al. are all shorter than those reported in [3], as the effect from collisional quenching by K atoms is neglected. Including the influence of potassium atoms but neglecting all other collisional partners except Ar yields a more general expression for the measured intensity ratio

$$R_{D-d} \propto \frac{a + bn}{c + dn}, \quad (3)$$

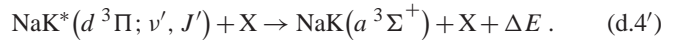
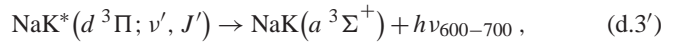
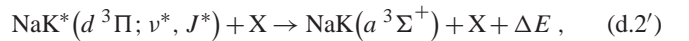
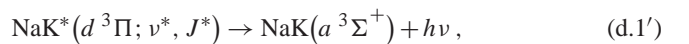
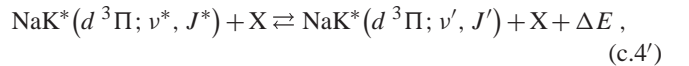
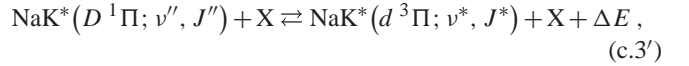
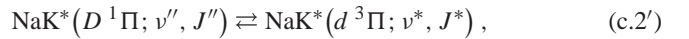
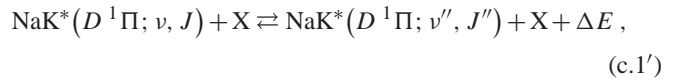
where the terms a and c include all factors not depending on the Ar pressure. Clearly, the inclusion of the potassium contribution does not significantly improve the situation. Thus, we must conclude that the simple model expressed in the reactions (a–d) and (3), and to an even larger extent (2), is not sufficient to describe the processes occurring in the studied system.

The minimal possible extension to the reactions (a–d) is to include one more state in the model. Two different plausible ways to do this exist. First, the initially excited state could couple as before to the triplet state and, in addition, couple to a third state, which is the one yielding the observed D -state emission. This model can be ruled out, however, as one of the transitions investigated in [1] involves the initially excited rovibrational state at 514.5 nm, $D(v=1, J=67)$ [4], which in this model would show the behaviour described

by (3). Second, a consecutive reaction scheme is very likely to be active in the present system. The reason for this is twofold. The initially excited $D(v, J)$ level is for all the transitions studied by Zhiwei et al. only weakly perturbed by the d state [3], which leads to a low probability of collisional energy transfer $D(v, J) \rightarrow d(v^*, J^*)$ [5]. Thus, to gain an appreciable chance to couple collisionally to the d state, the molecule first has to be transferred into a significantly perturbed level of the D state. The closest to the d -state strongly perturbed singlet-state level is $D(v=5, J=38)$, which couples to $d(v^*=4, J^*)$ [6]. Thus, the collisional energy transfer between the D and d states should involve an activation step, with an activation energy of a couple of hundred cm^{-1} , depending on the initial rovibronic D level. As shown below, inclusion of this consecutive step in the kinetic model is already enough to facilitate a good fit of the measured data.

Activation is not the only process that can influence the kinetics in the system. The second process contributing a consecutive step to the rate equations is collisional mixing of the $d(v^*, J^*)$ levels. Picking an arbitrary wavelength, as for example the 670 nm used by Zhiwei et al., for monitoring the $d(v', J') \rightarrow a$ radiative transition, means that the initial $d(v', J')$ state is ill-defined [7, 8] and in general not identical to the nascent state in the $D \rightarrow d(v^*, J^*)$ collisional transfer. Thus, even in the absence of an activation step, the observed triplet fluorescence will in the general case be the result of *at least* two collisions, one to bring the molecule from the D state to the $d(v^*, J^*)$ level and another one to populate the upper state $d(v', J')$ causing the observed $d \rightarrow a$ fluorescence.

To incorporate the consecutive scheme in the kinetic model of Zhiwei et al., we modify reactions (c–d) to read



In this modified scheme we have included the possibility of reverse reactions and we let X include K or Ar atoms. Setting up the full rate equations, making the steady-state assumption, and, assuming for simplicity only one of the above-mentioned consecutive steps to be present, the general expression for the measured fluorescence ratio becomes

$$R_{D-d} = \frac{a + bn + cn^2}{d + en + fn^2} \cdot \frac{A_d}{A_D}, \quad (4)$$

in which the parameters a – f are involved functions of all the rate constants for the modified reactions (a–d'). In Fig. 1, a fit of (4) to the experimental data points is displayed as the full

line, with fit parameters as given in the figure legend. Apparently, the experimental data is reproduced very nicely by (4), but the data set is too poor to produce a reliable fit of the six parameters and thus to facilitate an assessment of the validity of the assumed model. Even in the case of an extensive data set, however, there is clearly no possibility to extract any individual cross section from the fitted parameters, by just varying the Ar buffer gas pressure.

According to the argumentation above, the reaction mechanism is very likely to involve more than one intermediate step. The order of the polynomials in (4) will increase with one for every additional step, and they are thus most probably including cubic or higher terms of the pressure. As the data set was too limited already for a reliable fit of the one-intermediate-step model, we have to be content with noting that including terms of the pressure of higher order than two further improves the fit to the empirical data, but yields even less significant parameter values. It is thus, from the available data, not possible to tell whether more than one intermediate step is involved in the collisional energy transfer.

We have to conclude, unfortunately, that the method proposed by Zhiwei et al. in [1], to extract cross sections for collisional energy transfer between molecular states mediated by argon atoms, is neither correct nor suitable, as it fails to reproduce even qualitatively the observed molecular behaviour.

It is shown in this Comment that a model based on a consecutive scheme is likely to be correct and that a minimal assumption of one intermediate collisionally activated step is enough to satisfactorily reproduce the observations. However, the extracted parameters are functions of the involved rate constants too complex to leave any hope of attaining information on the desired cross sections, by just varying the argon buffer gas pressure in the fashion suggested by Zhiwei et al.

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