Rotational Energy Transfer within the A1 Σ⁺ u State of Na₂ Induced by Collisions with (2S1/2) Na

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The (v′ = 34, J′ = 14) level of the A1 Σ⁺ u electronic state of Na₂ has been selectively populated by excitation with the 578.1 nm line of a ring dye-laser with rhodamine 6G. Through collisions with (2S1/2) Na atoms, energy is transferred to neighbouring rotational levels in Na₂, and the density of these levels is determined by observing the fluorescence to the electronic ground state. From previous measurements of the lifetime of the A1 Σ⁺ u state and new measurements of the intensities of collision-induced spectral lines, absolute collision cross-sections for all rotational transitions up to ∆J = ±6 have been obtained; the total cross-section for all rotational transitions observed is: \( \sigma_{\text{total}} = 0.41 \text{ nm}^2 \).

Key words: Collisional Transfers; Cross-Section; Rotational Energy.

1. Introduction

In the last few years there has been renewed interest in the spectroscopy of alkali metal dimer molecules. These systems offer attractive possibilities for the study of many fundamental phenomena such as dissociation, perturbations, and curve crossings [1 – 3]. Besides, collision processes of these molecules can be conveniently and precisely studied using spectroscopic techniques. In favourable cases laser-induced fluorescence may be used to gain information about collisional processes.

Previously we have reported the results of the analysis of the fluorescence excited by a dye-laser at 17 297.387 cm⁻¹, which populates v′ = 34, J′ = 14 in A1 Σ⁺ u of sodium molecules (see [1]). We now present results of the absolute cross-section for rotational transitions to neighbouring rotational levels v′ = 34, J′ = 14 ± ∆J with ∆J = ±2, ±4, ±6.

2. Experimental

Fluorescence was excited by a ring dye-laser with rhodamine 6G (Spectra-Physics 380) delivering about 560 mW at 578.1 nm. Sodium vapour was contained in a heat-pipe at 760 K in the presence of argon at about 1.3 × 10⁴ Pa. Spectra were recorded by high resolution Fourier transform spectroscopy, and the dye-laser frequency was measured by a wave-meter and found to be 17297.387 cm⁻¹. The vapour pressure could be controlled by the temperature of the side arm, which was normally 527 °C, corresponding to vapour pressure \( P_{\text{Na}} = 0.8 × 10^4 \text{ Pa} \) and \( P_{\text{Na}_2} = 0.4 × 10^3 \text{ Pa} \) [4].

The argon pressure was measured with a capacitance membrane manometer. The temperature was measured with thermocouples. The sodium density \( n \) and mean velocity \( \bar{v} \) were calculated using the relation

\[ P = nkT \quad \text{and} \quad \bar{v} = \sqrt{\frac{8kT}{\pi \mu}}, \]

where \( \mu \) is the reduced mass of the colliding system. The dye-laser radiation overlaps with the transition R(13) in the 34-6 band of A1 Σ⁺ u − X1 Σ⁺ g and the collision-induced fluorescence lines (satellite lines) from neighbouring rotational levels (J′ + ∆J) are rather well resolved (Fig. 1). The identification of lines was made by calculating the satellite line wavelengths from the Na₂ molecular constants [5].

3. Method of Cross-Section Determination and Results

The method of obtaining the cross-section for collision-induced rotational transitions from the fluorescence...
cence spectrum has been described in [6]. The excited state \( \Sigma^+_u \) has a spontaneous lifetime \( \tau \approx 13 \) ns [7] and some of the excited molecules may undergo inelastic collisions with \( \Sigma^+_u \) Na atoms, resulting in transitions to neighbouring rotational levels \( J' + \Delta J \) in the \( v' = 34 \) level or to adjacent vibrational levels \( v' + \Delta v \). Transitions to other electronic states (e.g. the \( \Sigma^+_u \) state of \( \text{Na}_2 \)) are also possible, but with much smaller transition probabilities. The steady population \( N(\Delta J) \) of a rotational level \( J' + \Delta J \), in the excited \( \Sigma^+_u \) state, is determined by the following excitation and de-excitation processes:

(a) Collisional excitation: this can result either directly from the laser-excited level \( J \) [cross-section \( \sigma(\Delta J) \)] in a single collision, or by a second collision from neighbouring collisional populated levels \( \Delta J' \), if these levels collide again with \( \Sigma^+_u \) Na atoms before they radiate spontaneously [5].

(b) De-excitation: this may occur by spontaneous decay from level \( (J' + \Delta J) \) to the electronic ground state with the probability \( 1/\tau \), or by collisional energy transfer cross-sections \( \sigma_{\text{rot}}, \sigma_{\text{vib}}, \sigma_{\text{el}} \), respectively [8].

In general, the probability for two successive collision-induced transitions is small but detectable, and the possibility of more than two inelastic collisions of an excited molecule can be neglected completely. With this assumption the rate equation for the population of a level \( (J' + \Delta J) \) can be written as follows:

\[
\frac{dN(J)}{dt} = \left[ N(\theta)_{\text{rot}}\sigma(\Delta J) + \sum_{\Delta J'}''N(\Delta J')_{\text{rot}}\sigma(\Delta J - \Delta J') \right] n_{\text{Na}} \cdot \vec{v} \tag{1}
\]

\[-N(\Delta J) \left( \frac{1}{r} + \left( \sigma_{\text{rot}} + \sigma_{\text{vib}} + \sigma_{\text{el}} \right) n_{\text{Na}} \cdot \vec{v} \right),
\]

where \( \vec{v} \) is the mean relative velocity of the collision partners. The term \( \sum_{\Delta J'}''N(\Delta J')_{\text{rot}}\sigma(\Delta J - \Delta J') n_{\text{Na}} \cdot \vec{v} \) accounts for the increase of \( N(\Delta J') \) by a second collisional transition from all neighbouring rotational levels \( \Delta J' \). The summation, therefore, goes over all rotational excited levels (for which \( \Delta J = \theta \)) and the level \( \Delta J \) itself.

Equation (1) holds for each collisional populated level. Under steady state conditions \( \frac{dN(\Delta J)}{dt} = 0 \) and (1) presents a system of algebraic equations which are coupled by the \( \Sigma'' \)-term with the abbreviation

\[
\alpha = \left( -\frac{\sigma'' \sum N(\Delta J')_{\text{rot}}\sigma(\Delta J - \Delta J')}{N(\Delta J)} \right) n_{\text{Na}} \cdot \vec{v} \vec{r}.
\]

Equation (1) can be rearranged for steady state conditions with \( \frac{dN(\Delta J)}{dt} = 0 \):

\[
Q'(\Delta J) = \frac{N(\Delta J)}{N(0)} (1 + \alpha) = _{\text{rot}} \sigma(\Delta J)n_{\text{Na}} \cdot \vec{v} \vec{r}. \tag{2}
\]
Table 1. Experimental absolute cross-section for collision-induced rotational transitions.

<table>
<thead>
<tr>
<th>$\Delta J^{\text{rot}}$</th>
<th>$\sigma^{\text{exp}}(\Delta J)/\text{nm}^2$</th>
<th>$\Delta J^{\text{rot}}$</th>
<th>$\sigma^{\text{exp}}(\Delta J)/\text{nm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.05 ± 0.01</td>
<td>4</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>2</td>
<td>0.11 ± 0.03</td>
<td>−2</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>−4</td>
<td>0.05 ± 0.02</td>
<td>−6</td>
<td>0.03 ± 0.01</td>
</tr>
</tbody>
</table>

Fig. 2. Absolute cross-sections for all observed collision-induced rotational transitions $\Delta J$ in Na$_2$ with (2$S_{1/2}$) Na atoms.

At low pressure

$$Q(\Delta J) = \frac{N(\Delta J)}{N(0)} = \sigma^{\text{rot}}(\Delta J) n_{\text{Na}} \cdot \tau.$$ 

The quantity $Q = \frac{N(\Delta J)}{N(0)}$ can be determined from the measured fluorescence intensities $I(\Delta J)$ and $I(0)$ corrected by the Hönl-London factors for the R (and P) satellites [9–11]. The resulting absolute cross-section $\sigma^{\text{rot}}$ for collision-induced rotational transitions are presented in Figure 2. Numerical values of absolute cross-sections are listed in Table 1. The sum over all rotational transitions yields

$$\sigma^{\text{rot, total}} = \sum_{\Delta J = -6}^{6} \sigma^{\text{rot}}(\Delta J) = 0.41 \text{ nm}^2.$$ 

The inelastic cross-section $\sigma^{\text{rot}}(\Delta J)$ decreases rapidly with $|\Delta J|$ and $+\Delta J / -\Delta J$ asymmetry of cross-sections can be observed.

4. Conclusion

The investigation has shown that the technique of laser-induced fluorescence is well suited for the study of inelastic collision processes between electronically excited molecules and other collision partners. In Na$_2^* - \left(2S_{1/2}\right)$ Na the experimental cross-section has been determined for individual collision-induced transitions between well defined initial and final states, with reasonable accuracy.

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