# Collisional broadening of some $2^1\Delta_g \leftarrow B^1\Pi_u$ lines in $Na_2$ molecules by optical-optical double resonance spectroscopy

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Using the optical-optical double resonance (OODR) technique, we have studied the collisional broadening of some $2^1\Delta_g \leftarrow B^1\Pi_u$ lines in $Na_2$ molecules. A single line $Ar^+$ laser is used to pump the sodium dimers from thermally populated ground state $X^1\Sigma_g^+$ level to the intermediate $B^1\Pi_u$ state. Then, a single-mode diode laser is used to probe the doubly excited $2^1\Delta_g$ state. The broadening rate coefficient is determined from the slope of the total linewidth versus Ne density curve. We obtain the average value $k_{\rm br} = (1.1 \pm 0.5) \times 10^{-8}$ cm$^3$s$^{-1}$. The collisional excitation transfer between rotational levels of the $B^1\Pi_u$ state (i.e., $B^1\Pi_u(2, 83/84) \leftarrow B^1\Pi_u(2, 82)$) is also investigated. The rates can be determined from the relative intensities of the main peak and satellite lines, combined with a rate equation model. The rates of $1.25 \times 10^6$ and $1.07 \times 10^6$ s$^{-1}$ are obtained, respectively.

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In the past few years, photodissociation and collisional excitation transfer of alkali diatomic molecules have been extensively studied[1−6]. However, most previous spectroscopic studies have involved low-lying states correlating to the ground state and first excited state in the separated atom limit. The range of energies between the low-lying state and the Rydberg state has not been systematically investigated.

In this paper, we have used the optical-optical double resonance (OODR) technique to study the collisional broadening of some $2^1\Delta_g \leftarrow B^1\Pi_u$ lines of $Na_2$ molecules. In OODR, the first laser (pump) is used to populate one rovibrational level of an intermediate electronic state. The second laser (probe) is then used to excite these molecules to a higher electronic state. In our work, we have excited the ground state $X^1\Sigma_g^+$ to the high-lying state $2^1\Delta_g$ of $Na_2$ molecules by using the OODR technique. In the present case, collisional line broadening is dominated by collisions with Ne atoms, with a minor contribution from Na atom collisions. Specifically, dissociative collisions such as

$$Na_2(2^1\Delta_g) + Ne \rightarrow Na(5S) + Na(3S) + Ne, \qquad (1)$$

quenching collisions such as

$$Na_2(2^1\Delta_g) + Na(3S) \rightarrow Na_2(X^1\Sigma_g^+) + Na(5S), \qquad (2)$$

as well as elastic line broadening collisions contribute to the overall collision induced broadening linewidth. The collisional broadening rate coefficient is determined from the measured Doppler-free linewidth. The collisional excitation transfer between rotational levels of the $B^1\Pi_u(v', J')$ state is also investigated, and the collisional transfer rate for

$$Na_2[B^1\Pi_u(v, J)] + M \rightarrow Na_2[B^1\Pi_u(v, J')] + M, \qquad (3)$$

is measured, where $M$ represents the perturber which can be any of the species presented in the vapors (Ne, Na, $Na_2$).

The experimental setup is shown in Fig. 1. The sodium is contained in a cylindrical Pyrex cell with inner length of 15.0 cm and inner diameter of 2.5 cm using neon as a buffer gas. The cell is sealed after baking and evacuating to $10^{-4}$ Pa. The cell is placed inside an oven (not shown in Fig. 1), which is heated with a thermistor. The temperature is measured with several thermocouples located at various points on the cell. The temperature of the cell is less than 360 °C. The cell is connected by a narrow-bore tube and a greaseless stopcock to a vacuum and gas filling system from which neon gas is admitted as required. Neon pressures of 100—500 Pa are measured with a vacuum gauge. The density of sodium atoms in the vapor phase is obtained by measuring both the wing absorption coefficient and the ratio of the fluorescence to Rayleigh signal[7].

Two lasers are used to study the two-step excitation of $Na_2$ molecules. An all line visible $Ar^+$ laser (Shanghai, Aiao Laser Machinery Co. Ltd, using a prism to select one of the lines) is used to pump sodium dimers in

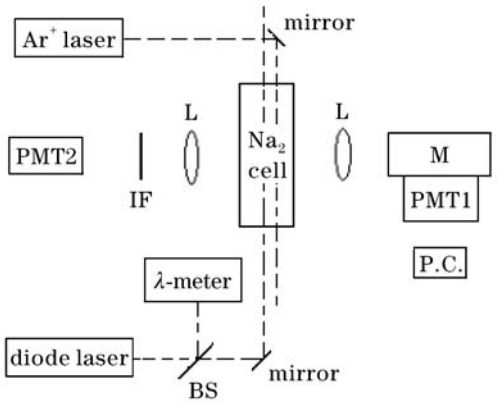


Fig. 1. Experimental setup. IF: interference filter; L: lens; M: monochromator; P.C.: photon counter; BS: beam-splitter; PMT: photomultiplier tube.

the thermally populated ground state levels to the intermediate $B^1\Pi_u$ state. A single-mode diode laser (Tuioptics, frequency range of 820—836 nm, power of 40 mW, linewidth of 5 MHz) is used to excite $Na_2$ molecules from the $B^1\Pi_u$ state to the $2^1\Delta_g$ state. In this experiment, the $Ar^+$ laser at 514.5 nm (120 mW, focusing the laser output into the portion of the sample cell produced a power density of about 3 W/cm$^2$) used as a pump laser to pump a specific level (2,82) of the $Na_2$ $B^1\Pi_u$ state from a level (6,83) of the $X^1\Sigma_g^+$ ground state[8], and the diode laser (the power density of about 1 W/cm$^2$) populates the $2^1\Delta_g$ level as $2^1\Delta_g(v,83) \leftarrow B^1\Pi_u(2,82)$. The two laser beams counterpropagate through the cell. The $2^1\Delta_g \rightarrow B^1\Pi_u$ fluorescence in the direction perpendicular to the laser beams is focused on the slits of 0.66-m monochromator (AM566, Acton), and monitored by a photomultiplier tube (PMT1). A photon counter (M1109, Prenceton) records the PMT signals. The total emissions consist of allowed transitions from the $2^1\Delta_g(v,83)$ level pumped through the two-step process to all possible $B^1\Pi_u(v',82/83/84)$. To record the OODR spectra, the violet fluorescence emitted from the excited triplet states, mainly $2^3\Pi_g$ and $3^3\Pi_g$, which are populated via collisions from $2^1\Delta_g$, to the $a^3\Sigma_u^+$ state is detected by a filtered photomultiplier tube (PMT2).

In the impact limit, which is appropriate for the conditions of the present experiment, the $Na_2[2^1\Delta_g(v,J) \leftarrow B^1\Pi_u(v',J') \leftarrow X^1\Sigma_g^+(v'',J'')]$ two-step Doppler-free absorption line shape is a Lorentzian function with full-width at half-maximum (FWHM) $\Gamma$, given by

$$\Gamma = \Gamma_{\rm p} + \Gamma_{\rm n} + k_{\rm br}^{\rm Ne} n_{\rm Ne} + k_{\rm br}^{\rm Na} n_{\rm Na}, \tag{4}$$

where, $\Gamma_{\rm P}$ is the predissociation linewidth, $\Gamma_{\rm n}$ is the natural linewidth of the transition, and $k_{\rm br}^i$ represents the broadening rate coeffcient, for a particular perturber species with number density $n_i$.

In this experiment, the density of the neon is $10^{16}-10^{17}$ cm$^{-3}$, while the density of atomic sodium is about three orders of magnitude smaller, so the broadening effect of sodium atoms can be neglected. Equation (4) can be reduced to

$$\Gamma = \Gamma_{\rm P} + \Gamma_{\rm n} + k_{\rm br}^{\rm Ne} n_{\rm Ne}. \tag{5}$$

For the $2^1\Delta_g(v,83) \leftarrow B^1\Pi_u(2,82)$ transition, we obtain the neon broadening rate coefficient $k_{\rm br}^{\rm Ne}$ from the dependence of the measured total linewidth $\Gamma$ on the neon gas density at fined temperature (fixed Na atom density). The line widths are measured by scanning the narrow-band $2^1\Delta_g(v,83) \leftarrow B^1\Pi_u(2,82)$ transition, while recording the molecular emission. The fluorescence line shape ($2^1\Delta_g(1,83) \rightarrow B^1\Pi_u(v',J')$) with $n_{\rm Ne} = 5.0\times10^{16}$ cm$^{-3}$ is shown in Fig. 2. The total linewidth $\Gamma$ is measured with an accuracy of about 30 MHz. Figure 3 shows the variation of linewidth with neon atomic density. Combined with Eq. (5), the measured total linewidth versus neon atomic density is well represented by a least squares fitted straight line, whose intercept and slope give $\frac{1}{\tau} = \Gamma_{\rm P}+\Gamma_{\rm n} = (2.5\pm1.1)\times10^9$ s$^{-1}$ ($\tau$ is the $2^1\Delta_g(v,J)$ state lifetime) and broadening rate coefficient $k_{\rm br}^{\rm Ne} = (1.1\pm0.5)\times10^{-8}$ cm$^3$s$^{-1}$, respectively. $k_{\rm br}$ only weakly depends on temperatures (i.e., $k_{\rm br} \propto T^{0.3}$[9]).

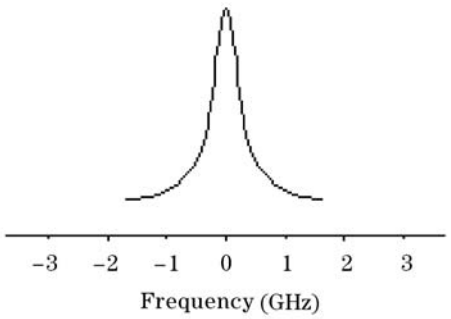


Fig. 2. Probe laser scans over $Na_2$ $2^1\Delta_g(1,83) \leftarrow B^1\Pi_u(2,82)$ transition. Molecular $Na_2$ ($2^1\Delta_g(1,83) \rightarrow B^1\Pi_u(v',J')$) fluorescence signal is monitored.

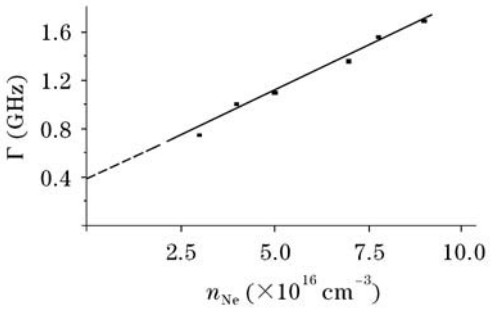


Fig. 3. Plot of the measured linewidth versus neon density for $2^1\Delta_g(1,83) \leftarrow B^1\Pi_u(2,82)$ transition.

Moreover, the sources of error in $k_{\rm br}^{\rm Ne}$ also involve the broadening effect of sodium atoms. We analogously obtain $k_{\rm br}^{\rm Ne} = (1.2\pm0.5)$, and $(1.0\pm0.5)\times10^{-8}$ cm$^3$s$^{-1}$ for the $2^1\Delta_g(2,83) \leftarrow B^1\Pi_u(2,82)$ and $2^1\Delta_g(3,83) \leftarrow B^1\Pi_u(2,82)$ transitions , respectively.

After the $B^1\Pi_u$ state has been prepared by pumping with a separate laser on a particular transition from the ground $X^1\Sigma_g^+$ state, we have observed collisional excitation transfer between different rotational levels of the $B^1\Pi_u$ state

$$B^1\Pi_u(v,J) + M \rightarrow B^1\Pi_u(v,J') + M, \tag{6}$$

where $M$ represents the perturber which can be any of the species presented in the vapors (Ne, Na, $Na_2$). The steady-state rate equation for the process of Eq. (6) is of the following form

$$R_{J\rightarrow J'} n_J = n_{J'}/\tau_{J'}, \tag{7}$$

where $R_{J\rightarrow J'}$ is the rate of population transfer from the $J$ to $J'$ level, and $\tau_{J'}$ is the lifetime of the $J'$ level, $n_J$ and $n_{J'}$ are the molecular densities of the $B^1\Pi_u(v,J)$ and $B^1\Pi_u(v,J')$ levels respectively. Equation (7) yields the ratio of the populations in the $J$ and $J'$ levels, $n_{J'}/n_J = R_{J\rightarrow J'}\tau_{J'}$. This ratio is approximately proportional to the fluorescence intensity ratio. Figure 4 shows the main line corresponding to the $2^1\Delta_g(1,83) \leftarrow B^1\Pi_u(2,82)$ transition, and the satellite peaks labeled $\Delta J = +1$ and $\Delta J = +2$ are identified as the $2^1\Delta_g(1,84) \leftarrow B^1\Pi_u(2,83)$ and $2^1\Delta_g(1,85) \leftarrow B^1\Pi_u(2,84)$ transition, respectively. From Fig. 4, we obtain the intensity ratio of 0.01 for the $\Delta J = +1$ ($J = 82 \rightarrow J' = 83$) excitation transfer collision, which yields $R_{J\rightarrow J+1} = (0.01)/\tau_{J+1}$. Since

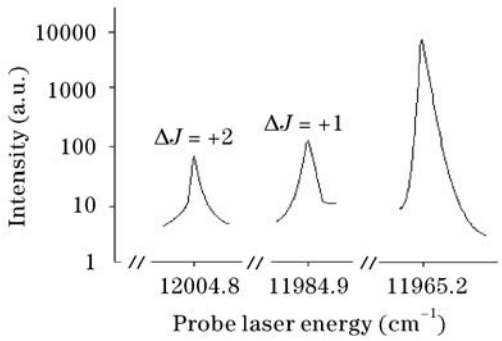


Fig. 4. Laser frequency scan showing the main line corresponding to $2^1\Delta_g(1,83) \leftarrow B^1\Pi_u(2,82)$ transition and the satellite peaks labeled $\Delta J = +1$ and $\Delta J = +2$.

$\tau_{J+1}$ is on the order of $8 \times 10^{-9}$ s, we obtain an approximate value $R_{J\rightarrow J+1} = 1.25 \times 10^6$ s$^{-1} \pm 45\%$. Similarly, we obtain $R_{J\rightarrow J+2} = 1.07 \times 10^6$ s$^{-1} \pm 45\%$. The major sources of error in these rates are uncertainties in the intensity ratios and in $\tau_{J'}$.

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