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Rovibrationally and Time-Resolved Radiative Lifetime and Collisional Cross Section Measurements of the $6^1\Sigma^+_g$(v=6, J=31) State of Molecular Sodium

Dinesh WAGLE
Miami University

Lok Raj PANT
Miami University

Joseph CONVERSE
Miami University

Scott WENNER
Miami University

Michael SAARANEN
Miami University

S. Burcin BAYRAM
Miami University

Abstract: In recent years, cold and ultracold alkali diatomic molecules have been at the forefront of quantum chemistry and manybody physics. Thus, there has been an increased interest in the determination of the radiative lifetimes for accurate knowledge of the transition dipole matrix elements of these molecules. In this work, we report on radiative lifetime measurements of the sodium diatomic molecule of the $6^1\Sigma^+_g$ (v=6,J=31) and $6^1\Sigma^+_g$ (v=8,J=31) molecular levels by a time-resolved laser spectroscopy technique. The ion-pair character of these potential energies makes their lifetimes interesting because of the unusual behavior of their transition dipole moments. The excitation to the Na_2 $6^1\Sigma^+_g$(3s+5s) electronic state was done using two synchronized pulsed lasers, directed to the sodium heatpipe oven, via $X^1\Sigma^+_g$ (v=0,31) → $A^1\Sigma^+_g$ (9,30) → $6^1\Sigma^+_g$ (8,31) and $X^1\Sigma^+_g$ (v=0,31) → $A^1\Sigma^+_g$ (7,30) → $6^1\Sigma^+_g$ (6,31) transition paths. Disperse molecular fluorescence decay time as a function of argon buffer gas was recorded using a time-correlated photon counting technique. Radiative lifetime was measured and collisional cross section between the excited sodium molecules and ground state argon atoms was extracted.

Keywords: Molecular physics, Spectroscopy, Lifetimes

Introduction

Alkali diatomic molecules have been compelling target for testing fundamental laws of nature and probing the new states of quantum matter to improve precision measurements of fundamental constants, and in the development of quantum information storage and molecule lasers [1-8]. Unlike other alkali dimers, sodium dimer has well separated rovibrational levels, thus it is relatively easier to optically probe the excited electronic states using visible laser light. Since the separation between the vibrational and rotational quantum levels of the sodium dimer are approximately 150 cm^{-1} and 10 cm^{-1} (1 cm^{-1} ≈ 30 GHz) respectively, the pulsed dye lasers are suitable for optical transitions. The study of potential energy curves for the ground and excited states of alkali molecule has always been the matter of interest in atomic, molecular and optical physics area [9,10]. The $6^1\Sigma^+_g$

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(3s+5s) state of Na_2 is of special importance because of the presence of a double well [11], with the secondary well locating at large internuclear distance, as shown in Fig. 1.

In our earlier work, we have reported the radiative lifetime measurement of the $6^1\Sigma^+_g$ (v=7,J=31) state and the calculations of radiative lifetimes in various rovibrational levels of the $6^1\Sigma^+_g$ (3s+5s) state. Our previous calculations revealed a large difference of about a factor of three between the $6^1\Sigma^+_g$ (v=40,J=1) and $6^1\Sigma^+_g$ (v=40,J=31) states due to the wavefunction alternating between having predominantly inner and outer well amplitude. In this work, we performed radiative lifetime measurements of the $6^1\Sigma^+_g$(v=6,J=31) and $6^1\Sigma^+_g$ (v=8,J=31) states of molecular sodium and extracted collisional cross sections. No experimental lifetime and collisional cross section data for these rovibrational levels exist in the literature.

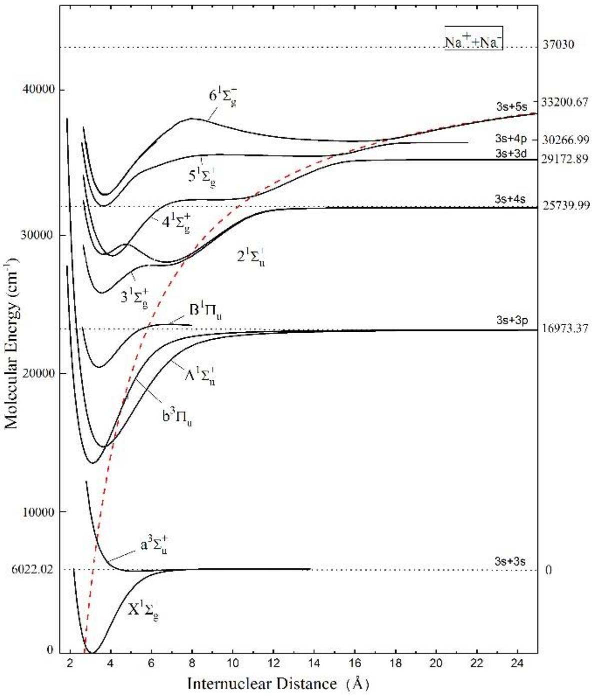

Figure 1. Partial potential energy curves of sodium molecule. The red dotted line represents the ion pair Na^+ + Na^- Coulomb interaction.

Experimental Methods

The experimental setup is shown in Fig. 2. The details of the setup were explained in our previous work [12], hence it will not be presented here. We used a four-armed heatpipe oven to heat sodium metal at desired temperature and pressure. The population of molecules in various rovibrational sates depends on temperature of the oven. The thermal population distribution in various rotational, $(2J+1)e^{-\frac{F(J)}{kT}}$, and vibrational, $e^{-\frac{G(v)}{kT}}$, quantum numbers in the $X^1\Sigma^+_g$ state between temperatures 300°C and 450°C are shown in Fig. 3. Here, F(J) and G(v) are the term values in terms of wavenumber, cm^{-1}. If the transition is initiated from the ground state having higher thermal population distribution of molecules, it is relatively easier to reach the desired rovibrational level (v,J). Two tunable pulsed dye lasers, pumped by a Nd:YAG laser operating in the second harmonics (532 nm) with a pulse repetition rate of 20 Hz, were used for the two-step excitation of sodium molecules into the $6^1\Sigma^+_g$ state. After the satisfaction of a double resonance condition a spectrometer-CCD/PMT system was used to identify the peaks and make lifetime measurements. The dispersed molecular fluorescence was measured at right angles to the propagation direction of the lasers and the signal was collected through a photomultiplier (PMT)-multichannel scalar (MCS) photon counting set-up.

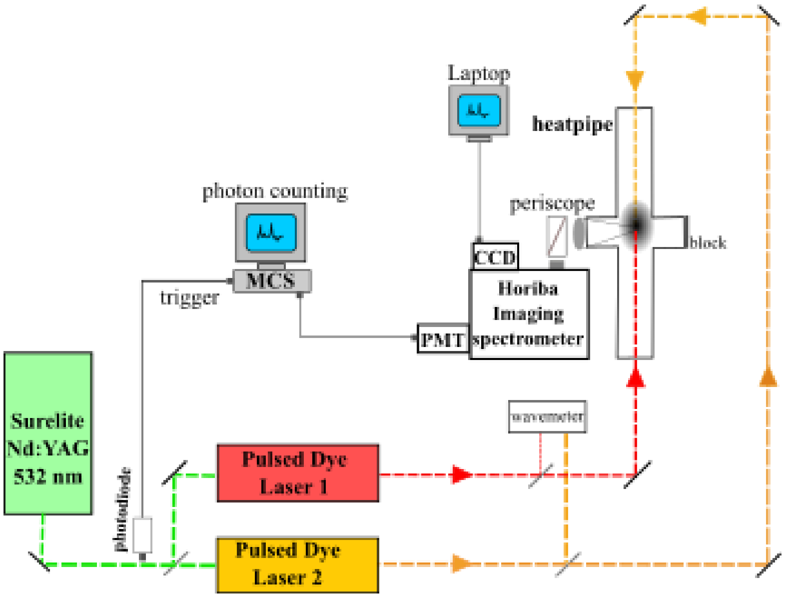

Figure 2. Experimental setup

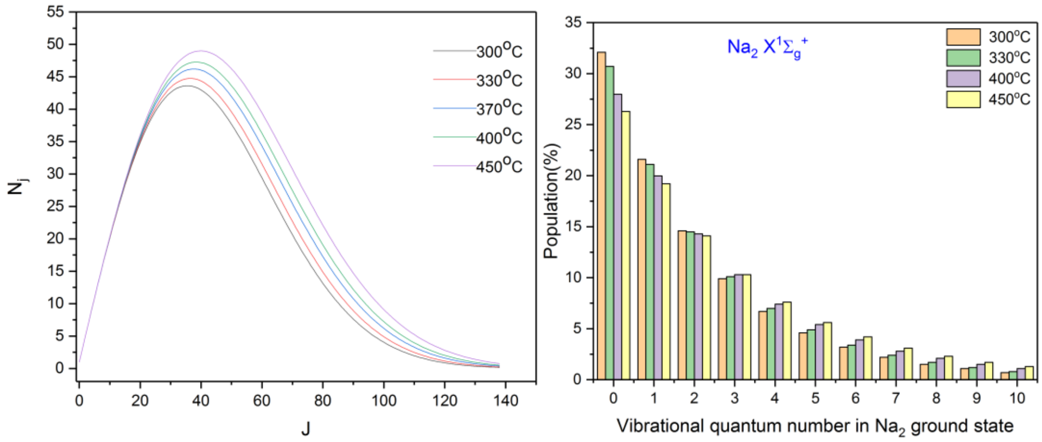

Figure 3. (Left) Rotational population distribution (N_j) as a function of rotational quantum number (J) in the ground state (B = 0.154 cm^{-1}), (Right) Relative thermal population as a function of vibrational quantum number

Lifetime Measurements of the $6^1\Sigma^+_g$ (v=6, J=31) and $6^1\Sigma^+_g$ (v=8, J=31) states of Na_2

The spectral peaks for the double resonance transition were identified using the Fortran LEVEL 8.0 program. In this program experimental potential energy curves are used to determine the Frank-Condon factors (FCFs), Einstein coefficients, energies of rovibrational levels, and dipole moment matrix elements. FCFs represent the probability of transition between two rovibrational states, and the intensity of peaks is proportional to FCF. The transition to excite the $6^1\Sigma^+_g$ (8,31) state is shown in Fig. 4. Due to high FCFs, the rovibrational levels (8,31) and (6,31) of the $6^1\Sigma^+_g$ state of Na_2 have been populated via the following resonant transitions:

$X^1\Sigma^+_g$ (v=0,31) → $A^1\Sigma^+_g$ (9,30) → $6^1\Sigma^+_g$ (8,31) and $X^1\Sigma^+_g$ (v=0,31) → $A^1\Sigma^+_g$ (8,30) → $6^1\Sigma^+_g$ (7,31).
Laser L_1 (1.8 mW power) drives the $X^1\Sigma^+_g$ (v=0,31) → $A^1\Sigma^+_g$ (9,30) transition at 639.84 nm, while laser L_2 (2.8 mW power) drives $A^1\Sigma^+_g$ (9,30) → $6^1\Sigma^+_g$ (8,31) transition at 561.80 nm. Similarly, for the excitation to the $6^1\Sigma^+_g$ (6,31) state, L_1 drives the $X^1\Sigma^+_g$ (v=0,31) → $A^1\Sigma^+_g$ (7,30) transition at 650 nm, while laser L_2 drives $A^1\Sigma^+_g$ (7,30) → $6^1\Sigma^+_g$ (6,31) transition at 561.80 nm. Both lasers are synchronized and the overlap time of the pulses are about 3 ns. After the two-step excitation a rovibrationally resolved molecular fluorescence spectrum from the $6^1\Sigma^+_g$ state was acquired. Figures 5 and 6 show fluorescence spectra from the $6^1\Sigma^+_g$ (6,31) and $6^1\Sigma^+_g$ (8,31) states. The double-resonance condition was confirmed by separately blocking the lasers. The spectrum shows P- and R- branches and the wavelengths for the peaks were identified comparing them with the theoretical values, obtained using LEVEL 8.0 Fortran program. High intensity of the spectral peaks suggest that the FCF of the

transition is higher. The FCF of the transitions at various wavelengths from the $6^1\Sigma^+_g$ (8,31) and $6^1\Sigma^+_g$ (6,31) state. The separation between the P- and R- branches of the doublets is approximately 13.40 cm^{-1}.

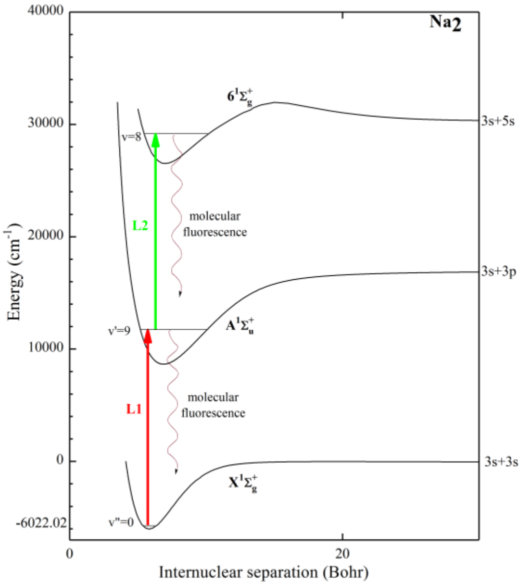

Figure 4. Partial energy curves showing excitation scheme for the $6^1\Sigma^+_g$ (8,31) state

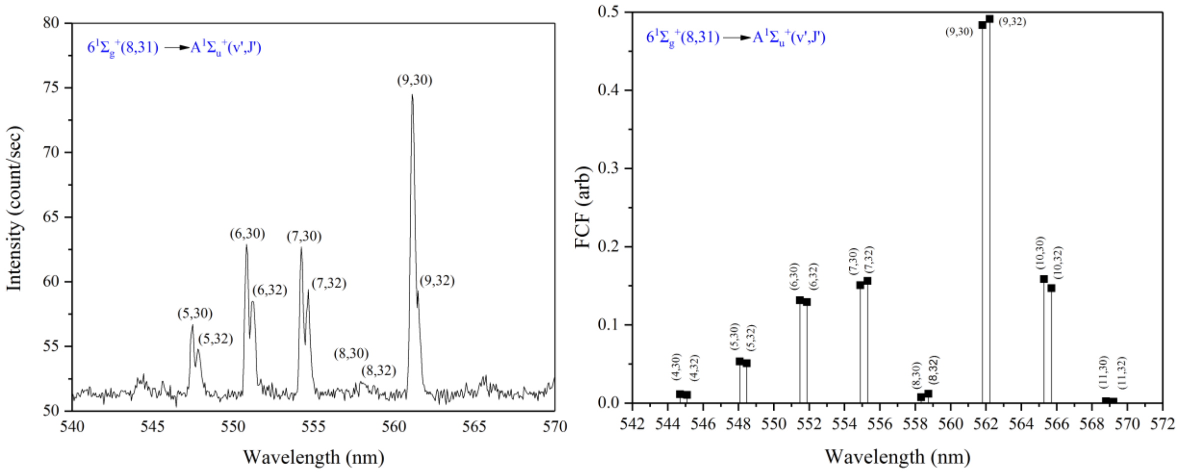

Figure 5. (Left) Molecular fluorescence, (Right) intensity spectrum showing relative Franck-Condon factors from the $6^1\Sigma^+_g$ (8,31) state to the $A^1\Sigma^+_g$ state

The typical decay signal of the $6^1\Sigma^+_g$ state as a function of time using time-correlated single photon counting method via multichannel scaler is shown in Fig. 7. The data shows the exponential drop of counts as a function of time where the red line is the convolution fit of a Gaussian with an exponential curve function. The effective lifetimes (τ_e) were extracted from the convolution fit using OriginLab 2017. Each data is the average of five measurements. Each measurement is the accumulation of 20000 scans. This process was repeated at various argon pressures. The inverse of the measured lifetimes were plotted against the corresponding pressures. This gives a linear relationship which is called Stern-Volmer plot as shown in Figure 8. The reciprocal of the intercept of the linear fit provides radiative lifetime. The radiative lifetime of the $6^1\Sigma^+_g$ (8,31) state is found to be 15± 1 ns at 300°C and that of the $6^1\Sigma^+_g$ (6,31) state is 13±1 ns at 330°C.

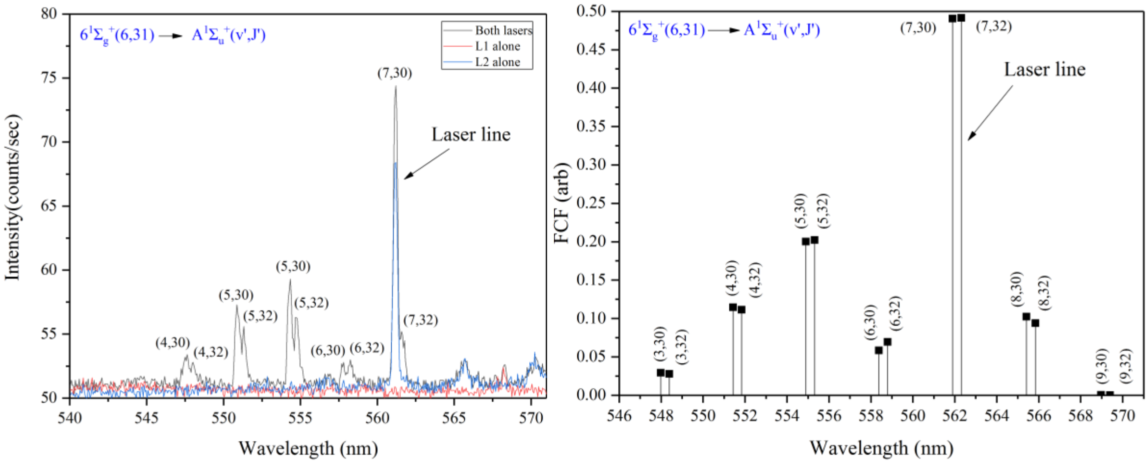

Figure 6. (Left) Molecular fluorescence, (Right) intensity spectrum showing relative Franck-Condon factors from the $6^1\Sigma^+_g$ (6,31) state to the $A^1\Sigma^+_g$ state

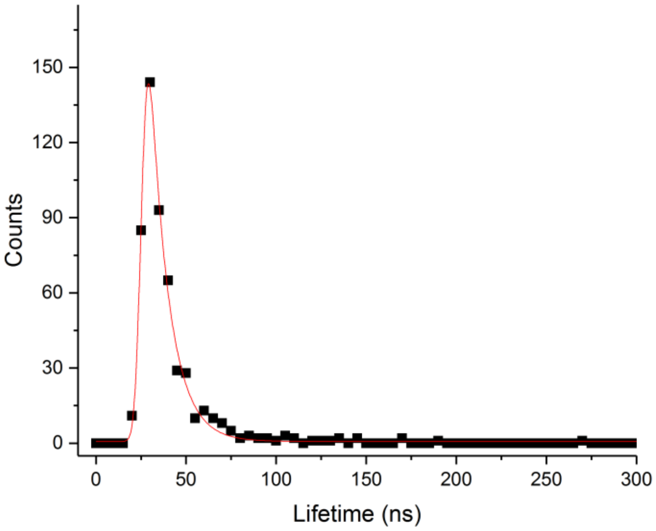

Figure 7. A typical lifetime measurement: the red line is a convolution fit of a Gaussian with an exponential curve function to the data.

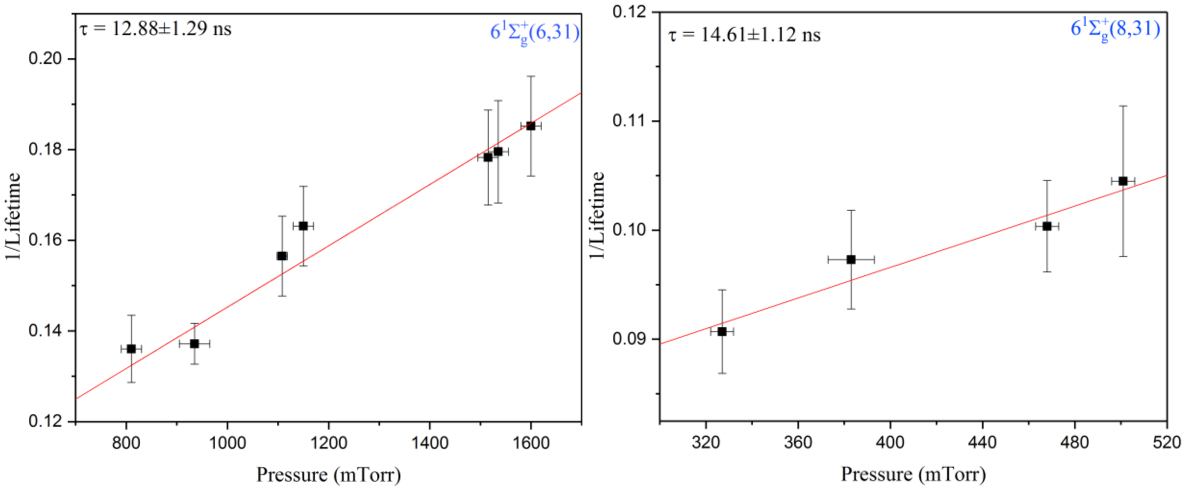

Figure 8. Stern-Volmer plots showing the variation in the inverse lifetimes as a function of Ar pressures

Collisional Cross Section

In the experiment, we used argon as a buffer gas and thus there are collisions among the sodium dimers, sodium atoms and argon atoms. As the argon pressure increases, the excited state sodium dimers may decay to other states by collisions. The collisional cross section of the excited state can be determined from the slope of the Stern-Volmer plot.

The effective lifetime (τ_e), radiative lifetime (τ_r) and non-radiative lifetime (τ_{nr}) are related by the Stern-Volmer relationship [13] which can be written as

$$\frac{1}{\tau_e} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}$$

where $\frac{1}{\tau_{nr}} = N_p \bar{v}\, \sigma.$ Here, N_p is the number density of the buffer gas, $\bar{v}$ is the average velocity of the colliding Na_2* - Ar atoms over the Maxwell-Boltzmann distribution of relative velocities at the heatpipe oven temperature, and σ is the collisional cross section between the excited dimer and Ar atoms. The number density of the buffer gas is determined by measuring the pressure at room temperature and applying the ideal gas law:

$$N_p = \frac{n}{V} = \frac{P}{\mathrm{RT}}$$

Also, average velocity is calculated using Maxwell-Boltzmann statistics:

$$\sqrt{\frac{8k_B T}{\pi\mu}}$$

Thus, the Stern-Volmer relationship reduces to the following:

$$\frac{1}{\tau_e} = \frac{1}{\tau_r} + \frac{\bar{v}}{\mathrm{k}_B T}\sigma P$$

The slope of the equation $(\frac{\bar{v}}{k_B T}\sigma)$ yields the collisional cross section while the intercept (1/ τ_e) at zero pressure yields the radiative lifetime.

The reciprocal of the intercept of the linear fit is the radiative lifetime. The radiative lifetime of the $6^1\Sigma^+{}_g$ (8,31) is measured to be 15±1 ns at 300°C and that of the $6^1\Sigma^+{}_g$ (6,31) state is 13±1 ns at 330°C. We measured the collisional cross section of the Na_2 $6^1\Sigma^+{}_g$ (8,31) state to be 555±100 $Å^2$ at 300°C and the $6^1\Sigma^+{}_g$ (6,31) state to be 546±56 $Å^2$ at 300°C.

Results and Discussion

We employed the technique of time-resolved spectroscopy to measure for the first the radiative lifetimes of the excited electronic states, $6^1\Sigma^+{}_g$ (8,31) and $6^1\Sigma^+{}_g$ (6,31) of sodium molecules. For the $6^1\Sigma^+{}_g$ state, the observed fluorescence is the result of double resonance molecular emission from the target rovibrational level. We have confirmed the peaks from the fluorescence emission with the results calculated using the LEVEL 8.0 Fortran program. Using a photon counting technique, we measured the effective lifetimes at various argon pressures and the radiative lifetime was extracted from the extrapolation of the linear fit to the zero pressure limit using a Stern-Volmer plot. Also, this plot is used to extract the collisional cross section at the operating temperature of the heatpipe. The obtained data are presented in Table 1. The measured radiative lifetimes of Na_2 $6^1\Sigma^+{}_g$ (v=8,J=31) and $6^1\Sigma^+{}_g$ (v=6,J=31) (even vibrational states) are in agreement within the error limits but both are smaller compared to the $6^1\Sigma^+{}_g$ (v=7,J=31) (odd vibrational state) [4]. Radiative lifetime oscillations in the Na_2 $4^1\Sigma^+{}_g$ state were reported [6].

Table 1. Tabulated data for radiative lifetimes (τ), temperatures (T), and collisional cross sections (σ)

State	τ (ns)	T (K)	σ (Å^2)	Source
$6^1\Sigma^+_g$ (8,31)	15±1	573	555 (100)	This work
$6^1\Sigma^+_g$ (7,31)	40±2	563	573 (35)*	Ref.[4]
$6^1\Sigma^+_g$ (6,31)	13±1	603	546 (56)	This work

*This work, which is calculated using experimental results from previous work [4]

It is possible, in principle, for the intermediate state molecules to be excited to a higher nearby rovibrational levels by collisions. The collisional kinetic energy depends on the k_BT, which is on the order of few hundred wavenumber. The separation between the rotational levels is about 13 cm^{-1} and the vibrational levels are 150 cm^{-1}. The shorter lifetimes for the v=6 and 8 states could be the perturbation in the intermediate A state due to the ion-pair state of sodium dimers. It is also possible for the molecules in the intermediate A state to be excited to a higher rovibrational levels by collisions. The shorter lifetimes maybe related to the excited state Na_2 collisions with the ground state iodine molecule or due to weak perturbations in the intermediate A state. Our results showed that the collisional cross sections for the excited $6^1\Sigma^+_g$ in the v= 6, 7, and 8 states are in excellent agreement within the error limits.

Conclusion

We employed the technique of time-resolved spectroscopy to measure the radiative lifetimes and collisional cross sections of the highly excited electronic states, $6^1\Sigma^+_g$ (8, 31) and $6^1\Sigma^+_g$ (6, 31), of sodium molecules for the first time. For the $6^1\Sigma^+_g$ state, the observed fluorescence is the result of double resonance molecular emission from the target rovibrational level. Using a photon counting technique, we measured the effective lifetimes at various argon pressures and the radiative lifetime was extracted by extrapolating the linear fit to the zero pressure limit of the Stern-Volmer plot. Further, a Stern-Volmer relationship is used to extract the collisional cross sections at the operating temperature of the heatpipe. The measured collisional cross sections for the v=6, 7, and 8 quantum states are found to be in excellent agreement within the error limits. The measured radiative lifetimes of Na_2 $6^1\Sigma^+_g$ (v=8,J=31) and $6^1\Sigma^+_g$ (v=6,J=31) (even vibrational states) are in excellent agreement with each other but both are smaller compared to the $6^1\Sigma^+_g$ (v=7,J=31) (odd vibrational state) [12]. Similar lifetime variations in the Na_2 $4^1\Sigma^+_g$ state were reported [14]. Hence, considerable differences in lifetimes for the v=6, 8 quantum numbers will be further investigated.

Recommendations

Prof. Noureddine Melikechi (atomic, molecular physics); E:mail: Noureddine_Melikechi@uml.edu
Prof. Mark Havey (atomic, molecular physics); E:mail: mhavey@odu.edu
Prof. Marjatta Lyyra (molecular physics); E:mail: lyyra@temple.edu
Prof. Gonul Basar (atomic spectroscopy); E-mail: gbasar@istanbul.edu.tr

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Author Information

Dinesh Wagle
Miami University
500 E. Street, 219 Kreger Hall,
Oxford, OH, 45056, USA
Contact E-mail: *wagled@miamioh.edu*

Lok Raj Pant
Miami University
500 E. Street, 219 Kreger Hall,
Oxford, OH, 45056, USA

Joseph Converse
Miami University
500 E. Street, 219 Kreger Hall,
Oxford, OH, 45056, USA

Scott Wenner
Miami University
500 E. Street, 219 Kreger Hall,
Oxford, OH, 45056, USA

Michael Saaranen
Miami University
500 E. Street, 219 Kreger Hall,
Oxford, OH, 45056, USA

Burcin Bayram
Miami University
500 E. Street, 219 Kreger Hall,
Oxford, OH, 45056, USA