EVIDENCE FOR PREDISSOCIATION OF Rb₂⁺(C¹Πₜₜ) INTO Rb⁺(2P₃/2) AND Rb⁺(2S₁/2)

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A nozzle beam of rubidium is irradiated by the 4765 Å line of the argon ion laser, and the resulting fluorescence is spectroscopically analyzed. Under these collision-free conditions, the emission consists of molecular fluorescence from the Rb₂ C¹Πₜₜ - X¹Σ⁺ electronic system as well as atomic fluorescence from the Rb⁺ 2P₃/2 fine structure component (the Rb D₂ line) only. The latter transition is caused by partial predissociation (∼25%) of the Rb₂ C¹Πₜₜ state. Within experimental error, the atomic fluorescence is not polarized and its intensity does not change when an electric field of 14.7 kV/cm is applied across the excitation region. The molecular fluorescence is polarized and has the value \( P = 0.345 \pm 0.009 \). This is interpreted to be caused by the superposition of P and R as well as Q lines. Although it is not possible to identify which state causes the predissociation of the Rb₂ C¹Πₜₜ state, arguments are presented that only the Rb D₂ line would appear provided the predissociation is an adiabatic process.

1. Introduction

Resonance fluorescence from alkali dimers has long been studied [1], but this topic has received renewed interest with the advent of visible laser excitation sources [2]. Recently, Brom and Broida [3] have investigated the emission resulting from rubidium vapor (1 - 100 torr pressure) when it is irradiated by various argon ion and krypton ion laser lines which pump the Rb₂ C¹Πₜₜ - X¹Σ⁺ band system. They found that the observed fluorescence spectrum had several unusual features, consisting of atomic emission at 7800 Å (Rb 5²P₃/2 - 5²S₁/2) and at 7948 Å (Rb 5²P₃/2 - 5²S₁/2), molecular emission from the Rb₂ B-X (6500 - 7500 Å) and A-X (7949 - 10 200 Å) band systems and a “quasi-continuum” (5400 - 6100 Å), as well as the expected resonance fluorescence series from the Rb₂ C-X band system. Moreover, they reported that the C-X fluorescence series consisted only of a progression of Q lines, although more than ten different series were excited.

It is well-known [4] that resonance fluorescence involving a A upper state and a Σ⁺ ground state should consist of either P and R line fluorescence series or a Q line series (u’ progression), the former from the Λ component labeled e and having the parity \((-1)^ζ\), the latter from the Λ component labeled f and having the (opposite) parity \((-1)^{ζ+1}\) [5]. These levels were previously labeled c and d, respectively. Although Brom and Broida found that the appearance of the overall emission spectrum was very dependent upon the vapor pressure of the metal, particularly the intensity of the quasi-continuum feature, the appearance of the Q line fluorescence series did not change with increasing vapor pressure. Brom and Broida conclude that the most reasonable explanation for the presence of only the Q line series is extensive predissociation of the e component of the C¹Πₜₜ Λ-doublet, that this predissociation is spontaneous rather than collision-induced, and that the predissociation is most likely caused by the A¹Σ⁺ state whose inner repulsive limb cuts through the C¹Πₜₜ state.

We report here a repetition of these studies using Rb₂ generated in a supersonic nozzle beam expansion rather than a heat pipe or cell. This has the advantage of permitting the investigation of the fluorescence of rubidium dimer as an essentially isolated molecule. The evidence gained from these beam experiments supports and confirms some of the above conclusions, but casts doubt on others. The atomic and molecular fluorescence was studied as a function of polarization and as a function of applied electric field. From these studies we suggest that the mechanism for predissociation of the Rb₂ C
state involves interaction with either the \( \text{Rb}_2 \) A or B states, both of which correlate in the separated atom limit with \( \text{Rb}^{2P}_{3/2} \).

2. Experimental

The apparatus used to generate the nozzle beam of \( \text{Rb}_2 \) molecules has been described in detail previously [6,7]. The beam is formed in a double oven consisting of a body and a nozzle chamber, surrounded by liquid-nitrogen-cooled shrouds. The oven is filled with a 25 g ampoule of rubidium (Kawecki-Berylco Industries, Inc., 99.5% purity). During a typical run the body chamber is maintained at a temperature of about 850 K corresponding to a rubidium vapor pressure of about 120 torr [8]. In order to prevent clogging, the nozzle chamber is kept about 100 degrees higher than the body. The background pressure of the system is maintained at about \( 5 \times 10^{-6} \) torr.

The nozzle beam expands into a large Pyrex belljar (16.8 cm diameter) equipped with four sidearms. The light beam from the 4765 Å line of a multimode cw argon ion laser intersects the nozzle beam at right angles, producing visible fluorescence approximately 12 cm downstream from the nozzle source. In this region free molecular flow exists. The fluorescence is detected at right angles to both the nozzle beam and laser beam and resolved by a 1 m Czerny–Turner scanning spectrometer (Interactive Technology, Inc.) having a cooled Centronic Q 4283 photomultiplier (S-20 extended red response) attached to its exit slits.

For the polarization studies of the molecular emission, the laser beam is linearly polarized with its electric vector parallel to the direction of the nozzle beam. The fluorescence is viewed by an uncooled EMI 6256 QA photomultiplier having an interference filter (30 Å FWHM, centered about 4880 Å) placed in front of it. This filter isolates the (6,9), (6,10) and (6,11) members of the Q-line fluorescence series. It also reduces the scattered light and blocks the atomic fluorescence. The analyzing polarizer consists of a pair of matched Polaroid sheets mounted on a sliding frame [7]. One sheet allows measurement of \( I_\perp \), the other \( I_\parallel \), in order to calculate the degree of polarization,

\[
P = (I_\perp - I_\parallel)/(I_\perp + I_\parallel).
\]

The measurement of the degree of polarization of the atomic fluorescence differs from the above in the replacement of the 4880 Å interference filter by a 7800 Å interference filter (12 Å FWHM) and by the use of a cooled RCA 31034 (128 response) photomultiplier.

The electric field studies are carried out with the help of a larger belljar (21.5 cm diameter). The Stark plates are mounted on an adjustable, insulated stand which is in turn balanced on four nipples blown into the belljar. The plates are separated 1.6 cm by boron nitride spacers. To avoid deposition of the alkali metal on the plates and spacers, additional copper collimators are attached to the liquid-nitrogen-cooled shields. A Spellman DC high voltage power supply (RHR-30P10), capable of delivering 30 kV, is used. The laser intersects the beam at 45° and the field at 90°. The molecular fluorescence, isolated by the 4880 Å filter, is detected in the same plane as the nozzle and laser beams but at right angles to the laser beam.

For comparison purposes, fluorescence is also excited in a pyrex cell containing Rb vapor. The cell consists of a body with four windows mounted at right angles and a separately-heated finger containing a rubidium reservoir which controls the vapor pressure in the cell body.

3. Results and discussion

3.1. Comparison of beam and bulb fluorescence

All three argon ion laser lines available to us (4765 Å, 4880 Å, and 5145 Å) cause fluorescence in the rubidium vapor cell but only the 4765 Å line produces detectable fluorescence in the nozzle beam of rubidium. This observation is not surprising since the 4765 Å line pumps predominantly the \( \nu'' = 1 \) level of \( \text{Rb}_2 \), the 4880 Å line the \( \nu'' = 8 \) level and the 5145 Å line the \( \nu'' = 35 \) level [3,9]. Because of the extensive vibrational cooling of the \( \text{Rb}_2 \) dimers in the nozzle beam [6], one would not expect to find an appreciable population of the \( \text{Rb}_2 \) high vibrational levels.

The 4765 Å line pumps mainly the \( \text{Rb}_2 \) C–X \( \nu'' = 1 \rightarrow \nu' = 6 \) transition. The resulting fluorescence from the nozzle beam consists of what appeared to be a series of Q lines and the \( \text{Rb} \) 5p \( ^1P_{3/2} - 5s \) \( ^2S_{1/2} \) atomic line (7800 Å). Unlike the case for the \( \text{Rb} \) cell, the \( \text{Rb} \) 5p \( ^2P_{1/2} - 5s \) \( ^2S_{1/2} \) atomic line (7947 Å) is absent (see fig. 1). There is also no evidence for the A–X and B–X
emission in the Rb beam or the quasi-continuum feature, all of which had been detected earlier in the cell and in the heat pipe. Our findings support the conclusion that these emissions are caused in the cell by collisional energy transfer and are not a primary photo-process.

Conversely, the appearance of the Rb D₂ line upon irradiation of the nozzle beam of Rb₂ dimers by the 4765 Å laser line is established as caused by the absorption of the pump light without the inversion of subsequent collisions. The intensity of the Rb D₂ line is found to be proportional to the intensity of the 4765 Å laser line (see fig. 2), thus ruling out multi-photon processes as the source for the atomic emission here [10]. Moreover, the 4880 Å laser line does not cause the appearance of atomic emission in the nozzle beam (although it does in the bulb), thus ruling out photodissociation. Hence it is concluded that predissociation of the Rb₂ C state is responsible for the appearance of the Rb D₂ line. Based on the best estimate of the Rb₂ ground state dissociation energy [9], the translational energy of the newly-formed Rb⁺(2P³/₂) atom is calculated to be 0.25 eV.

3.2. Polarization of atomic fluorescence

In general, the angular distribution of photofragments is anisotropic [11]. In particular, if one of the photofragments is in an excited state, the emission should be polarized and the degree of polarization will depend on the intrinsic degree of polarization of the radiative transition, \( P_0 \), and the asymmetry of the fragment angular distribution \( \beta \). Consequently, the degree of polarization of the Rb D₂ line was measured. However, the value for \( P \) was found to be \(-0.020 \pm 0.019\), i.e., the Rb D₂ emission line appears to be unpolarized.

For a \(^2P_{3/2} \rightarrow ^2S_{1/2}\) atomic transition, theory [12] shows that the maximum degree of polarization of the atomic fragment expected from photodissociation is

\[
P = \frac{3\beta/(20 + \beta)}{P_0},
\]

where \( \beta \) is the asymmetry parameter [coefficient of \( P_2(\cos \theta) \)] and \( P_0 \) is the intrinsic polarization. Equation (2) is for the dissociation of a \(^2\) state; the dissociation of a \( ^1 \) state yields an even smaller value of \( P \). For Rb₁, \( P_0 \) is about 0.21 [13] while \( \beta \) has the range \(-1 < \beta \leq 2\). Thus the maximum value of \( P \) that could occur is about 0.057. If the predissociating state has a lifetime com-
parable to the rotational period of the excited state, this value will be further reduced. Unfortunately, therefore, it is not possible to determine the form of the angular distribution of the photofragments in this case from the present measurement of $P$.

3.3. Polarization of molecular fluorescence

The measurements of the degree of polarization for the molecular emission pumped by the 4765 Å laser line yield unexpected results. In the classical (high $J$) limit for Rb$_2$ molecules being excited and their fluorescence being detected with the geometry as described, one would expect $P = 0.5$ for Q lines, i.e., for $(Q\uparrow, Q\downarrow)$ resonance fluorescence [14]. The value measured for Rb$_2$ is $P = 0.345 \pm 0.009$. This value of $P$ suggests two possibilities (1) the emission is a Q line for $J = 1$ for which $P = \frac{1}{2}$; or (2) the emission is some average of the classical value of $P$ for Q line emission ($P = \frac{1}{2}$) and $P$ and R line emission ($P = \frac{1}{2}$), depending upon the relative strengths of the different Q line and P and R line fluorescence series excited. The first possibility is ruled out since we have observed that $P$ varies as a function of observed emission wavelength. Consequently, we are led to question Brom and Broida's conclusion that the molecular fluorescence consists only of Q lines. A more thorough study by Tam and Happer [15] has shown the existence of P and R lines as well as Q line emission. Consequently, we conclude from these polarization measurements that the Rb$_2$ C $^1\Pi_u$ state is only partially predissociated. Moreover, the fact that the value for $P$ we obtained by observing the total molecular fluorescence is so close to that expected from a simple superposition of the polarization of P and R lines with Q lines suggests that this predissociation is rather weak. By measuring the relative intensities of the atomic fluorescence to the molecular fluorescence under the collision-free conditions of our beam experiment, we place an upper bound of 25% on the percentage of Rb$_2$ C state molecules that predissociate before they fluoresce.

3.4. Search for electric field mixing of the $\Lambda$ components

In an electric field, parity is no longer a conserved quantity. We investigated the possibility that the application of an electric field would mix the two $\Lambda$ components of the $^1\Pi_u$ state, causing more molecules to predissociate if only one of the $\Lambda$ components is connected to the continuum. This would result in a decrease in the intensity of the molecular emission and an increase in the intensity of the atomic emission. Previously, this type of experiment had been performed successfully on the heteronuclear molecule NaK by Drullinger, Hessel and Smith [16]. Upon excitation of a P or R line, they observed the strength of the Q line to grow and the P and R lines to diminish as the electric field was increased. In order to expect similar results for a homonuclear molecule, there must be some relaxation of the nuclear symmetry selection rules, i.e., some mixing of ortho and para states. For the "mixed dimer" $^{85}$Rb$^{87}$Rb, ortho and para symmetry is not defined, but for this type of molecule the excited state dipole moment is expected to be quite small. In the case at hand, the application of a 15 kV/cm electric field is found to be insufficient to cause this mixing to be detectable, or the mixing does not enhance the predissociation rate.

3.5. Possible predissociation mechanisms

Although no rotational analysis has been performed on the Rb$_2$ C state, it is assigned to be a $^1\Pi_u$ state based on comparison with other alkali dimers. This assignment is further supported by the presence of P and R as well as Q lines. The only other reasonable choice is a $^3\Pi_u$ state, but the short radiative lifetime ($\sim 14 - 19$ ms)
ns) of this state \([17]\) causes us to dismiss this possibili-

Fig. 3 presents a correlation diagram showing how the states of the separated atoms (one excited and one unexcited) first transform into Hund's case (c) states of the diatomic molecule and then into Hund's case (a) states. The ordering of the case (a) states used here follows Mulliken's recommendations \([18]\). For Hund's case (a) or (b) the selection rules for predissociation are \(g = u, \Delta S = 0,\) and \(\Delta \Lambda = 0 \pm 1 \[4\].\) This narrows the possible states responsible for predissociating the C state to the states \(A \, 1 \Sigma_u^+\) and \(B \, 1 \Pi_u.\) We note from fig. 3 that both these states correlate with the separated atoms \(\text{Rb} \, 2P_{3/2} + \text{Rb} \, 2S_{1/2}.\)

Interaction of the \(C \, 1 \Pi_u\) state with the \(A \, 1 \Sigma_u^+\) state would affect only one of the \(A\) components, while interaction with the \(B \, 1 \Pi_u\) state would predissociate both \(A\) components. From the fact that both \(P\) and \(R\) as well as \(Q\) lines are present and have the relative intensities that are expected for an unperturbed system, we are led to doubt that the \(A \, 1 \Sigma_u^+\) state is responsible for causing the predissociation seen. We cannot, though, rule it out because the extent of predissociation is weak.

So far we have concentrated our attention on predissociation allowed by the case (a) selection rules. However, the selection rule \(\Delta S = 0\) may be violated (weak predissociation). Thus, we must also consider the possibility that the \(3 \Pi_u\) or the \(3 \Sigma_u^+\) states may be responsible for predissociating the \(C \, 1 \Pi_u\) state. Fig. 3 suggests that the \(3 \Pi_u\) state would cause the appearance of both \(\text{Rb} \, D_1\) and \(D_2\) emission lines. Hence we reject this possibility. However, the same arguments cannot eliminate the \(3 \Sigma_u^+\) state from consideration.

It is important to note that this correlation assumes that the \(A \, 1 \Sigma_u^+\) and the \(B \, 1 \Pi_u\) state lie above the \(3 \Pi_u\) state. We discuss here what evidence there exists for this ordering. First of all, the \(B\) state is known spectroscopically to lie above the \(A\) state. It is also known that the \(A \, 1 \Sigma_u^+\) state of the alkali dimers shows a magnetic rotation spectrum \([19,20]\) and recently Kusch and Hessel \([21]\) have observed perturbations in the \(A \, 1 \Sigma_u^+\) state of \(\text{Na}_2\) caused by the presence of the \(3 \Pi_u\) state, thus confirming the suggestion by Carroll that the interaction of the \(A \, 1 \Sigma_u^+\) state and the \(3 \Pi_u\) states were responsible for the magnetic rotation spectrum. It appears that the relative ordering can be deduced from an analysis of the perturbations in the \(\text{Na}_2 \, A \, 1 \Sigma_u^+\) state and preliminary results \([22]\) from this study suggest that this ordering is as illustrated in fig. 3. The most recent pseudopotential calculation by Bardsley, Junker and Norcross \([23]\) also shows that the minimum of the \(3 \Pi_u\) state lies lower than the minimum of the \(A \, 1 \Sigma_u^+\) state in agreement with Mulliken's proposed ordering. Thus, although it appears that we presently have insufficient information to conclude which state causes the observed predissociation, fig. 3 shows that emission from the \(\text{Rb} \, 2P_{3/2}\) fine structure component is expected provided the predissociation proceeds in an adiabatic manner.

3.6. Some implications of \(\text{Rb}_2^+\) predissociation

It is difficult to produce a uniform distribution of excited Rb atoms in a dense vapor of rubidium. Optical excitation by a Rb resonance lamp will not suffice for this purpose since the Rb \(D_1\) and \(D_2\) lines are strongly absorbed close to the surface of the Rb vapor. However, the present study shows that excitation of the \(\text{Rb}_2\) molecules present in the vapor by the lines of the argon ion laser readily yields \(\text{Rb}_2^+\) \(2P_{3/2}\) atoms with relatively high translational energy because the \(\text{Rb}_2 \, C \, 1 \Pi_u\) state is predissociated. This may make possible the utilization of various physical and chemical processing schemes that are based on the use of \(\text{Rb}_2^+\) as a reactant.

For example, Letokhov and Ambartzumian \([24]\) have proposed a two-step photoionization process for the separation of the Rb isotopes. Alternatively, one might employ the photopredissociation scheme of Moore \([25]\) provided an efficient scavenger of \(\text{Rb}_2^+\) is found. Experiments by Tam, Moe, and Happer \([26]\) have shown that \(\text{H}_2\) might be such a scavenger. They report the formation of micron-sized particles when rubidium vapor in the presence of 150 torr or more of \(\text{H}_2\) gas is excited by the 4880 \(\AA\) and 4765 \(\AA\) lines of the argon ion laser, and they suggest that rubidium is a good candidate for laser isotope separation by this technique. The present demonstration that \(\text{Rb}_2^+\) atoms can be generated in optically dense vapors of rubidium may also have relevance to various proposed laser devices based on the use of dense alkali vapors \([27,28]\).

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References

[22] M.M. Hessel, private communication.