A Li/Li₂ Supersonic Nozzle Beam*

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ABSTRACT

The characterization of a lithium supersonic nozzle beam has been made using spectroscopic techniques. It is found that at a stagnation pressure of 5.3 kPa (40 torr) and a nozzle throat diameter of 0.4 mm the ground state vibrational population of Li_2 can be described by a Boltzmann distribution with $T_v = 195 \pm 30^\circ\text{K}$. The rotational temperature is found to be $T_r = 70 \pm 20^\circ\text{K}$ by band shape analysis. Measurements by quadrupole mass spectrometer indicates that ~ 10 mole per cent Li_2 dimers are formed at an oven body temperature of 1370°K in the supersonic nozzle expansion. This measured mole fraction is in good agreement with the existing dimerization theory.

I. Introduction

The molecular beam reaction program developed in our laboratory has included experiments involving a high-energy (~ 5 eV) H atom beam (1) colliding with a Li/Li₂ supersonic beam. This paper reports the characterization of the Li/Li₂ cross beam.

The characterization of supersonic beams of the heavier alkalis has been extensively studied. (2-7) Gordon, Lee, and Herschbach (5) (GLH) studied K₂, Rb₂ and Cs₂ by utilizing techniques such as the analysis of velocity distribution and magnetic deflection. Forman, Kendall, and Grice (6) (FKG) studied K₂ by employing the same techniques as GLH. Sinha, Schultz, and Zare (7) (SSZ) studied Na₂ and K₂ by using spectroscopic techniques such as white-light and laser-induced fluorescence. We have studied Li₂ by the white-light fluorescence technique and have measured the mole fraction of Li₂ by mass spectrometry. In the studies of Rb₂, Cs₂, and K₂, GLH and FKG have indirectly shown the evidence for the existence of the vibrationally hot dimers. However, SSZ found no evidence for the presence of such vibrationally hot dimers in Na₂ and K₂, although under their experimental conditions 10% to 40% of the Na₂ dimers present were formed downstream of the nozzle. According to the simple one-dimensional theory of dimerization introduced by GLH, it is these dimers formed downstream that are believed to be vibrationally hot because of infrequent collisions.

In our Li₂ experiment we arrived at the same conclusion as SSZ did, that is, the vibrational population of the dimer nozzle beam can be described by a Boltzmann distribution. Due to the thermochemical properties of elemental lithium, the atomic vapor pressure is only 13.3 kPa (100 torr) even at an oven body temperature of 1370°K. The dimer mole fraction was

measured to be 10% of which only 2% was formed downstream of the nozzle.

II. Experimental

The primary molecular beam apparatus (I) used in this experiment is the collision chamber of our primary beam apparatus (I). The background pressure remains ≤ 3.3 mPa (2.5×10^{-5} torr) during the run. The interaction region of the light and molecular beam is 7.6 cm downstream from the nozzle. In a second beam apparatus (II), there is differential pumping between the oven chamber and the detection chamber such that a background pressure of 0.13 mPa (1×10^{-6} torr) in the detection chamber can be obtained during the run. The distance in II between the interaction region and the nozzle is 66 cm. The white-light source is a 150 W Xe-Arc lamp. The geometry of optical arrangement is similar to that used by SSZ. The resulting fluorescent spectra were taken by a 0.5 - m Jarrell Ash spectrometer. A 100 μ slitwidth corresponding to a resolution of 0.14 nm in the visible region was used. The fluorescence intensities were measured either with a Bendix channeltron tube 8X-7500-5103 (S20) or with a RCA 1P 28 (S5) photomultiplier. The photoelectric signal was detected with a PAR model 134 electrometer and finally displayed on a strip-chart recorder.

Li metal was obtained from Alfa products. The intensity of ^7Li atom and dimer beams were measured by a UTI model 100C quadrupole mass spectrometer with a sensitivity (Faraday cup) of 1.1×10^{-5} A/Pa (1.5×10^{-3} A/torr). The electron multiplier was normally operated at a gain of 1×10^5 (attained with an emission current of 2.5 mA). The mass spectrometer is situated perpendicular to the nozzle beam and is 22 cm away from the oven nozzle in apparatus I.

The 304 stainless steel oven is similar in design to others, e.g., GLH; one has a nozzle throat diameter of 0.43 mm, the other 0.36 mm. The nozzle

erosion was found to be of no significant importance under the present experimental conditions. Runs were carried out for oven body temperatures between 1230 to 1370 °K, corresponding to Li atomic vapor pressures of 3.3 - 13.3 kPa(25-100 torr). The temperature difference between oven nozzle and oven body was varied from 50 to 130°C. Within these ranges of experimental conditions, the measured relative band intensities do not show significant differences. However, most of the runs were carried out at a stagnation pressure of 5.3 kPa (40 torr).

We have also made several runs for Na₂ in apparatus II, typically at oven body temperatures of 980°K, corresponding to 13.3 kPa Na atomic vapor pressure inside the oven. Spectra obtained were essentially the same as those reported by SSZ. Therefore, no further analyses were made.

III. Results and Discussions

A. Vibrational Temperature

A typical Li_2 B $^1\Pi_u \rightarrow \text{X } ^1\Sigma_g^+$ fluorescence spectrum obtained by white-light excitation is shown in Figure 1. Spectrum 1(a) was taken from the supersonic nozzle beam with a nozzle throat of 0.36 mm, and with oven body and nozzle temperatures of 1280 and 1430°K, respectively. Spectrum 1(b) was taken from a heatpipe oven with 26.6 kPa (~ 200 torr) He buffer gas. The heatpipe was operated at a temperature of 910°K. The remarkable cooling effect due to the nozzle expansion is evident in both the vibrational and rotational structure of the dimer spectra. It should be noted that in the heatpipe oven the gas pressure was of the order of 26.6 kPa, and thus the relative band intensities were slightly affected by collision - induced transitions, whereas in the supersonic nozzle beam the background pressure was lower than 2.6 mPa (2×10^{-5} torr), and thus collision-induced processes are negligible. Therefore, the relative integrated intensities of the vibrational bands in Figure 1(a) reflect the relative population of excited vibrational levels, which is, in turn, populated by the absorption of the white-light source from the supersonic nozzle beam. Table I lists some of the measured band intensities.

The analysis of the vibrational temperature was made in the same manner as SSZ. Molecular constants of B state (8) and X state (9) were taken from the literature. The Franck-Condon factors, $q_{v',v''}$, were calculated by the RKR method using the computer program of Zare (10). A constant electronic transition moment was assumed throughout the calculations. The relative excited state populations, $N_{v'}$, were determined according to eq. (2) of SSZ after a correction for detection response (i.e., the spectral efficiency of

spectrometer and spectral response of the photomultiplier} in the measured intensities. Once $N_{v'}$ had been determined, the vibrational population of the ground state Li_2 can be calculated. Using SSZ's eq (3), with the right hand side multiplied by the corrected lamp intensity at $\nu(\nu'v'')$, and setting $\nu_{\max} = 2$, we were able to obtain the ground state vibrational population, $N_{v''}$. Results for $N_{v'}$ and $N_{v''}$ are also included in Table I. It is found that those $N_{v''}$ can be described by a Boltzmann distribution with a vibrational temperature of $195 \pm 30^\circ\text{K}$. The standard deviation, which arises mainly from the measured band intensities and spectral response of the detection system, is the combined uncertainty of the two sets of data obtained by two photomultipliers used in our experiments.

B. Rotational Temperature

The rotational cooling is remarkable as can be seen by comparing the band shapes in Figure 1. To determine the rotational temperature, we matched the calculated band contour with the experimental one.

The relative rotation-vibration line intensities are given by (8)

$$I(\nu', J'; \nu'', J'') = K \frac{B_{\nu'}}{T_r} g_{J''} S_{J''}^{J'} \nu^4(\nu'J'; \nu''J'') \exp\left(-\frac{hc F(J')}{k T_r}\right) \quad (1)$$

where K is a proportionality constant; $\nu(\nu'J'; \nu''J'')$ is the frequency of the emission line; $B_{\nu'}$ is the rotational spectroscopic constant for vibrational level ν' ; T_r is the rotational temperature; and g_J is the statistical factor due to nuclear spin. ^7Li has a nuclear spin of $3/2$, thus $g_{J''} = 1/(2I+1)$ for even J'' ; and $g_{J''} = (I+1)/(2I+1)$ for odd J'' . $F(J')$ is the rotational term value for vibrational level ν' , and $S_{J''}^{J'}$ is the Honl-London factor. For the electronic transition of the type $^1\Pi \rightarrow ^1\Sigma$, the Honl-London factors are $S_{J''}^{J'} = (J''+2)/4$ for R-branch; $S_{J''}^{J'} = (2J'' + 1)/4$ for Q-branch; and $S_{J''}^{J'} = (J''-1)/4$ for P-branch.

The theoretical band contours were calculated for various assumed rotational temperatures by convoluting a spectral slit function with the relative intensities of all rotational lines within a 100 nm range containing the band head. The calculated band contours of the (0,0) band for three rotational temperatures are given in Figure 2, where the experimental band shape is also included. Rotational quantum numbers up to $J=100$ were initially included, but it was soon found that for a rotational temperature of the order of $T_r = 70^\circ\text{K}$, only $J \leq 30$ were needed for the calculation. As can be seen from Figure 2 it was possible to determine rotational temperature to within 20°K .

The same procedures were carried out for (1,0) and (0,1) bands. The rotational temperature of this Li_2 nozzle beam in each case was determined to be $T_r = 70 \pm 20^\circ\text{K}$. If one makes the reasonable assumption that the rotational temperature is in equilibrium with the translation temperature, then the Mach number of our nozzle beam is calculated to be 6.7 to 7.5 for the conditions studied.

C. Dimer Mole Fraction

The relative beam intensities of Li atom and dimer were measured by quadrupole mass spectrometer. It was found that the Li_2 mole fraction increased from 2 to 10% when the stagnation pressure was varied from 1.06 kPa to 13.3 kPa. This is in good agreement with that calculated for the alkali dimer mole fraction as a function of reduced variables by GLH. Under our experimental conditions the reduced variables are $\bar{T} = 0.1$, $\bar{w} = 40-50$, and $\bar{p} = 3.5 - 9 \times 10^{-6}$. Accordingly, at 1370°K , ~8% of the 10% dimers formed originated in the oven, only the remaining ~2% of them were formed downstream from the nozzle.

D. Absolute Intensity

The absolute intensity of the supersonic beam was estimated (assuming unit sticking probability on a cooled surface) to be (within an order of magnitude) 4×10^{18} atoms/sr-sec (using quantitative titration) for the following stagnation conditions:

$T = 1370^\circ\text{K}$, $P_{\text{total}} = 13.3 \text{ kPa}$ (100 torr), nozzle diameter = 0.35 mm.

IV. Conclusion

Remarkable temperature cooling of Li_2 beams due to supersonic expansion has been observed. The analysis shows that the vibrational and rotational temperature freezes out at different rates. Under our experimental conditions vibrationally hot Li_2 dimers were not detected because the dimers originated mainly inside the oven.

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Table I. Typical data for Li_2 nozzle beam taken using a Bendix channeltron tube. The calculated relative populations of the excited state, $N_{v'}$, and the ground state, $N_{v''}$, are also included.

Band (v', v'')	Measured I ($v'v''$) (arbitrary units)	Frequency $\nu(\text{cm}^{-1})$	$q_{v'v''}$	Response of detection system	Excited State $N_{v'}$	v	Ground State $N_{v''}/N_{0''}$
(0,0)	1.0	20398.50	0.3194	0.172	1.051	0	1
(0,1)	1.165	20052.27	0.3810	0.177	1.068		
(1,0)	1.12	20662.49	0.3378	0.165	1.102	1	5.50×10^{-2}
(1,2)	0.485	19975.26	0.1501	0.179	1.133		
(2,0)	0.345	20920.42	0.2027	0.160	0.555	2	8.00×10^{-3}
(2,1)	0.177	20574.19	0.1001	0.167	0.591		
(2,2)	0.240	20233.19	0.1308	0.175	0.626		

Figure Captions

Figure 1. The ${}^7\text{Li}_2$ B ${}^1\Pi_u + X$ ${}^1\Sigma_g^+$ fluorescence spectrum excited by white light in (a) a supersonic nozzle beam with oven body and oven nozzle temperatures of 1280 and 1430°K, respectively, and (b) a heatpipe oven with 26.7 kPa He added at a temperature of 910°K. The vibrational bands are identified by (v',v'') .

Figure 2. The comparison of theoretical band contours of the $(0,0)$ band, calculated for three rotational temperatures, and the experimental contour. The hump at 492 nm in the experimental contour is due to the $(1,1)$ band.

Figure 1.

Figure 2.