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Light-induced shifts in chemical equilibria: Optical orientation-induced shift in 2Li(*g*)⇌Li$_2$(*g*) and ortho/para enrichment

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The shift in the equilibrium distribution between reactants and products in the chemical reaction 2Li⇌Li$_2$ that accompanies an optical orientation of the atomic Li spin angular momentum has been observed, and its dependence and degree of atomic orientation is reported. An examination of the resolved rotational structure in the Li$_2$ electronic spectrum reveals the production of molecular nuclear spin polarization that accompanies the equilibrium shift, resulting in a change in the *ortho/para* ratio for Li$_2$. Orientation of the spin angular momentum of the $2\,^2S_{1/2}$ ground state Li atoms was produced in a vapor cell by optical pumping with a tunable, single mode cw dye laser, and the molecular density in different rotational states of the ^{2}Li$_2$ $X\,^1\Sigma_g^+$ ($v = 0$) molecular state was monitored using a second cw dye laser.

INTRODUCTION

Twenty-five years ago it was pointed out that light can shift the point of equilibrium in a chemical reaction mixture.[1] Optical orientation of the atomic spins in an atom–dimer reaction mixture will shift the equilibrium to favor the atomic species. This prediction is based on the known electronic multiplicity of the bonding and antibonding molecular electronic states which correlate with the ground state atoms. Specifically, the interaction of two spin-oriented (the same M_J state) $^2S_{1/2}$ atoms follows a spin-triplet, antibonding collision trajectory, while the bonding $X\,^1\Sigma_g^+$ state is correlated with mixed atomic M_J levels. Of course, third body collisions must also occur in order to remove energy in order to stabilize the bond formation. The number of $^2S_{1/2}$ atom–atom collisions that can lead to bond formation is diminished in a spin-oriented vapor. If the various molecular dissociation processes remain unchanged, the net result is a shift in the atom–molecule vapor composition in the direction of increased atom density. The rate constant for the molecule formation step is decreased, while that for molecular dissociation is unchanged. The alkali metal vapors are excellent candidates for the observation and study of this effect since large spin orientations can be produced in the presence of inert buffer gases, and molecular densities can easily be monitored with visible radiation. As a practical consideration, inert buffer gases such as He have very low spin disorientation cross sections in collisions with alkali atoms, resulting in long spin relaxation times in the presence of several hundred Torr of buffer gas. Experimental tests of the shift hypothesis can, therefore, be carried out in buffered vapor cells, where the degree of orientation can approach 100%.

Subsequently, this effect received attention from several research groups. In the late 1960s Kastler pointed out how the shift should depend upon the degree of atomic orientation.[2] Alzetta *et al.* made the first experimental observation of the shift in a mixture of potassium and sodium vapors.[3] Weber and Stock observed the shift in Na vapor and also detected the presence of nuclear spin polarization in the Na$_2$ molecules.[4] Allegrini *et al.* examined the functional relationship between the shift and the atomic orientation in Na–K mixtures and in pure Na vapor.[5,6] All of these early experiments used the accidental coincidence between the frequency of some gas or ion laser line with a molecular transition to monitor the change in molecular density and are reviewed by Bicchi.[7] More recently, the shift was observed in Cs vapor by Ho *et al.*[8] where a tunable dye laser was used to scan over a molecular band in order to measure the equilibrium shift. The above considerations are also important for the stabilization of spin-polarized hydrogen atoms.[9]

In the present work, the shift is studied for the 2Li⇌Li$_2$ reaction in the presence of a He buffer gas. This is a particularly interesting situation because the well-resolved rotational structure of the molecular electronic spectrum can be monitored as a function of atomic orientation. The shift in *ortho/para* ratio as well as the shift in reaction equilibrium can be followed simultaneously in one experiment by scanning over a section of the rotationally resolved spectrum.[10]

EXPERIMENTAL

The experimental requirements include two laser sources, one to produce the atomic Li orientation and the other to monitor the Li$_2$ molecular density as well as the *ortho* and *para* concentrations of Li$_2$. The atomic Li orientation is produced in a vapor cell using the optical pumping configuration first introduced by Dehmelt,[11] where circularly polarized D_1 resonance radiation at 670 nm propagates through the cell parallel to an applied magnetic field. Orientation consists of preferred population of one of the magnetic sublevels with either maximum or minimum M_F in the ground electronic state of Li. The molecular
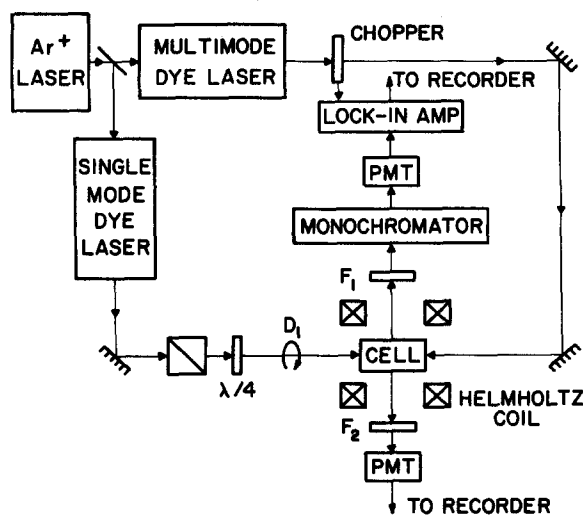
FIG. 1. A schematic representation of the experimental arrangement used to produce Li atomic spin orientation and detect shifts in Li_2 molecular density and *ortho/para* ratio.

FIG. 2. The dependence of Li atomic spin orientation on incident power of the D_1 optical pumping radiation for two cell temperatures.

density and rotational state distributions of Li_2 are monitored with a second tunable cw dye laser propagating counter to the atomic optical pumping laser in the vapor cell. The radiation from this second laser is chopped at 1300 Hz to permit lock-in detection of the molecular fluorescence signal. A 0.25 m monochromator–filter combination (Jarrell–Ash 82-410 and Corion 790) is used to reject light at the Li D_1 frequency and pass molecular fluorescence in a 750–810 nm band, where it is then detected by a photomultiplier (Hamamatsu R928). A schematic of the experimental arrangement is shown in Fig. 1.

The vapor cell consists of a stainless steel pipe cross, 1.86 in. i.d., filled at room temperature with isotopically pure (99.9%) ^7Li and 200 Torr helium buffer gas (6.4×10^{18} atoms/cm^3). The buffer gas pressure was chosen to permit the production of a broad range of atomic orientation parameters in the temperature range for which accurate molecular density measurements can be made. In the present case, this was 592–623 K. The cell was heated with electrical heating tape and the temperature measured with a chromel–alumel thermocouple.

Both dye lasers utilized a 1.5×10^{-3} M concentration of DCM dye in a 40%–60% benzyl alcohol–ethylene glycol solvent. The optical orientation dye laser (Coherent 599-21) was operated stabilized on single mode, while the molecular detection dye laser was operated multimode and scanned.

A steady magnetic field of 38.9 G was applied to the cell with a pair of 12 in. diameter Helmholtz coils. This field is of sufficient magnitude to overcome disorientation effects due the stray time-dependent magnetic fields arising from the current through the heating tape. Without the steady applied magnetic field, atomic orientation could not be produced. The atomic orientation was determined from the intensity of D_1 resonance fluorescence collected at 90° to the excitation light and passed through a 12 nm bandwidth interference filter centered at 670 nm (F_2 in Fig. 1). The orientation parameter is defined as
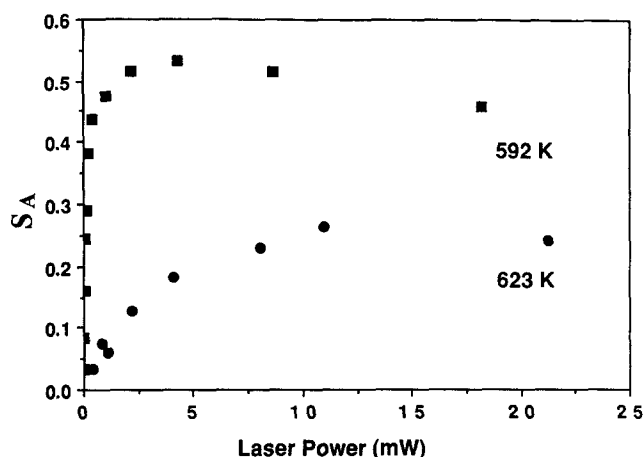
$$S = [I(H=0) - I(H)]/I(H=0), \tag{1}$$

where $I(H)$ and $I(H=0)$ are the D_1 resonance fluorescence intensities measured in the presence and absence, respectively, of the steady applied magnetic field. For the cell geometry, pumping light intensities, and temperatures used, self-absorption of the D_1 light introduces little error in the determination of S. This is confirmed by measurements of S from the transmitted D_1 radiation in the Dehmelt-type experiment which gave agreement with the fluorescence procedure.

The degree of atomic Li orientation is dependent upon incident pumping power and temperature of the vapor cell as illustrated in Fig. 2. It is interesting to note the low optical pumping powers at which the maximum orientation can be achieved. For example, a value of $S = 0.53$ can be produced with only 4 mW of D_1 light in a beam diameter of 3.2 mm and with a helium buffer gas density of 6.4×10^{18} cm^{-3} at 592 K. However, in the present experiment the shift was studied at a cell temperature of 623 K, where the maximum atomic orientation that can be produced is only $S = 0.26$, but where the change in molecular densities in the rotationally resolved (2–0) band can be measured under conditions of good S/N. At 623 K, the vapor pressures of Li and Li_2 are calculated to be 1.16×10^{-5} and 1.8×10^{-8} Torr,[12] respectively, yielding an equilibrium constant $K_P = 1.01 \times 10^5$ atm^{-1} for $2Li(g) \rightleftharpoons Li_2(g)$ at 623 K.

RESULTS AND DISCUSSION

A small segment of the excitation spectrum of Li_2 is recorded with $S = 0$, which is the condition that exists in the cell when the static applied magnetic field is turned to zero. When the applied field is turned on to 38.9 G, with its direction parallel to the circularly polarized atomic optical pumping radiation $S \neq 0$ and the same segment of the Li_2 excitation spectrum is scanned again. The results are shown in Fig. 3 for a segment that is mainly composed of $A\,^1\Sigma_u^+\,(v=2) - X\,^1\Sigma_g^+\,(v=0)$ transitions and a value of $S = 0.2$. Some lines are blends of several transitions, but
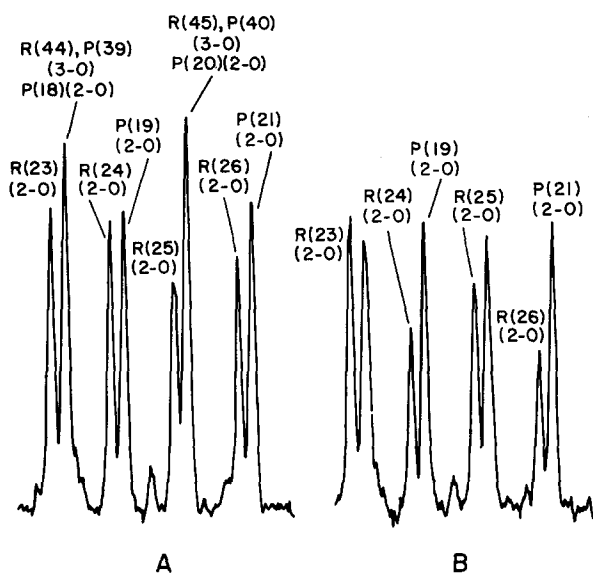
FIG. 3. A segment of the $^7Li_2$ $A\ ^1\Sigma_u^+ - X\ ^1\Sigma_g^+$ laser-induced fluorescence spectrum: (A) in the absence of ^7Li atomic spin orientation and (B) in the presence of ^7Li atomic spin orientation with an orientation parameter $S = 0.2$, showing the change in several $X\ ^1\Sigma_g^+$ ($v = 0$) rotational level populations.

TABLE I. The dependence of observed $A\ ^1\Sigma_u^+ - X\ ^1\Sigma_g^+$ $^7Li_2$ spectral line intensities upon optical pumping laser power and ^7Li atomic spin orientation for several ground state ($v = 0$) rotational levels taken from the spectral region covered in Fig. 4.

D_1 laser power (mW)	S_A	Para		Ortho			
		$\Delta(24)$	$\Delta(26)$	$\Delta(19)$	$\Delta(21)$	$\Delta(23)$	$\Delta(25)$
0.140	0.030	0.104	0.145	0.000	0.026	−0.024	−0.014
0.360	0.043	0.253	0.243	−0.024	0.000	−0.064	−0.028
0.760	0.063	0.412	0.372	0.031	0.059	0.026	−0.009
1.760	0.105	0.433	0.418	0.059	0.036	0.039	0.078
3.400	0.162	0.436	0.442	0.051	0.008	0.031	0.060
7.000	0.220	0.450	0.453	0.072	0.069	0.063	0.059
14.800	0.258	0.486	0.476	0.024	0.006	0.022	0.081

The dependence of these changes on the degree of atomic orientation was measured for several ground state rotational levels, and the results are given in Table I and summarized in Fig. 4 where the shift in molecular density is

$$\Delta = \frac{F_M(S_A=0) - F_M(S_A)}{F_M(S_A=0)}.$$

$F_M(S_A = 0)$ is the molecular laser-induced fluorescence intensity measured at zero atomic orientation ($S_A = 0$), and $F_M(S_A)$ is the molecular laser-induced fluorescence intensity measured at the value of atomic orientation given by S_A. It is immediately evident, e.g., that the shift in the population of the $X\ ^1\Sigma_g^+$ ($v = 0$, $J = 26$) level exhibits a decrease with increasing atomic orientation, leveling out at a value of $\Delta = 0.45$. Not all of the transitions are included in Fig. 4 because of uncertainties remaining because of blends.

On the other hand, the ortho state populations in the small segment of molecular spectra used in this experiment are little changed with increasing atomic orientation. The para states behave similarly and exhibit a decrease in population, while the ortho states also behave similarly, but
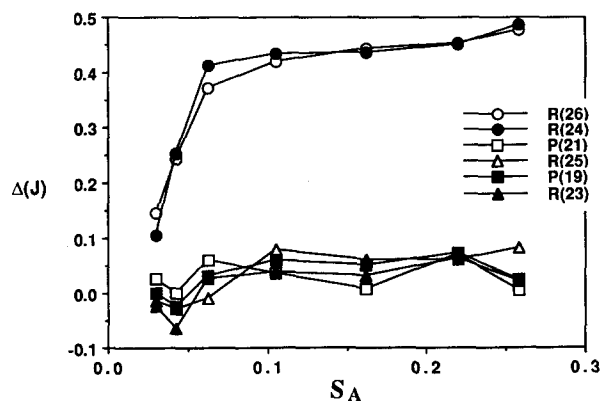
there are others which give a clearly resolved measure of the change in population of several $X\ ^1\Sigma_g^+$ rotational levels that accompany the atomic spin orientation.

Several features are immediately evident. Transitions which originate from *even J* rotational levels in the ground $X\ ^1\Sigma_g^+$ state *decrease* in intensity upon production of Li atomic orientation. These are *para* molecular species having total nuclear spin $T = 2$ or 0, since the ^7Li nuclear spin is $I = 3/2$. Transitions which originate from ground state levels with *odd* values of J retain nearly the same intensity in the presence of Li atomic orientation in the example shown in Fig. 3. These are *ortho* molecules having total nuclear spin $T = 3$ or 1. The spectral lines that are blends of transitions from *ortho* and *para* states decrease in intensity. The overall change in molecular density can be found by averaging the intensities of the completely resolved transitions from *ortho* and *para* levels of the $X\ ^1\Sigma_g^+$ state of $^7Li_2$.

These results can be explained as arising from a combination of two effects. First, the total molecular density decreases upon introduction of an atomic orientation in agreement with the original prediction of a shift in the point of equilibrium for the reaction $2Li \rightleftharpoons Li_2$. Second, the ortho/para ratio increases due to production of nuclear spin orientation in the Li_2 molecules. In this respect, the results have some similarity to the previously observed situation in Na vapor.[4] The $T = 3$ *ortho* modification of $^7Li_2$ is favored at the expense of the other molecular nuclear spin states. This can result from (a) oriented Li atoms chemically exchanging with Li atoms in the dimer and/or (b) the effects of atomic electron–molecular nuclear spin exchange interactions in addition to recombination of partially oriented atoms.

FIG. 4. The shift Δ for several completely resolved rotational lines in the $A\ ^1\Sigma_u^+$ ($v = 2$)$-X\ ^1\Sigma_g^+$ ($v = 0$) transition for $^7Li_2$ as a function of atomic ^7Li spin orientation.
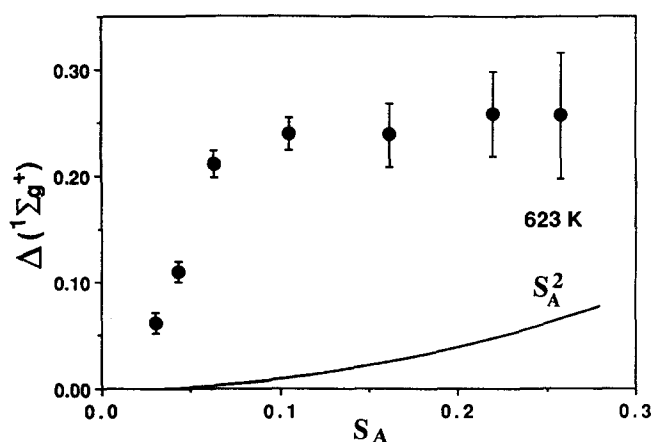
FIG. 5. The average shift in $^7Li_2$ molecular density with ^7Li atomic spin orientation S together with the S^2 dependence predicted by the simple two-level model.

show little shift. If the results for the *ortho* states are averaged and then further averaged with the average for the *para* states

$$\Delta(X\,^1\Sigma_g^+) = \langle\langle\Delta(ortho)\rangle + \langle\Delta(para)\rangle\rangle,$$

then an average shift in molecular density of ground state dimers $\Delta(X\,^1\Sigma_g^+)$ is obtained. This is shown in Fig. 5 for the limited data that originate from cleanly resolved transitions.

A number of years ago Kastler pointed out[2] that the apparent equilibrium constant for a $2X \rightleftharpoons X_2$ alkali dimerization reaction should depend upon the degree of atomic orientation as

$$K(T,S_A) = K(T,0)(1 - S_A^2),$$

where $K(T,S_A)$ is the equilibrium constant at temperature T and atomic orientation parameter S_A for a hypothetical atom with only two M levels $M = \pm 1/2$. In terms of the present definitions for molecular shift, $\Delta(X\,^1\Sigma_g^+)$ is predicted to be equal to S_A^2 if the Kastler relation holds. While there appeared to be agreement with the S_A^2 dependence for previous observations on other vapors,[6] it is absent here in lithium vapor as can be seen from Fig. 5 where a plot of $\Delta(X\,^1\Sigma_g^+)$ vs S_A^2 is also given. The evident disagreement may be due to several sources. In the first place, ^7Li is not a two-level $M = \pm 1/2$ system. In fact, the ground atomic state has two hyperfine states with M_F levels ranging from $+2$ to -2 for $F = 2$, and $+1$ to -1 for $F = 1$. Moreover, the values of S_A used here are defined operationally in terms of the intensity of the atomic fluorescence and do not reflect the complete details of the population distribution over either the M_F levels or the hyperfine states. A meaningful discussion of the dependence of shift on atomic orientation would have to incorporate these considerations. The population distribution over M_F could be measured in a radio frequency resonance disorientation experiment at magnetic fields sufficiently large enough to produce quadratic splitting.

CONCLUSIONS

First of all, it is clear that a shift in the equilibrium concentration of molecular $^7Li_2$ has occurred in the presence of an optical spin orientation of ^7Li atoms. The enrichment of the *ortho*-lithium dimers is a second result. Moreover, the determination of the increase in *ortho/para* ratio is accomplished here by means of a simultaneous measurement on the *ortho* and *para* molecules in one spectral scan. All previous shift studies, with the exception of that in cesium,[8] were performed using accidental coincidences between a cw laser line and a molecular transition and, therefore, may be sensitive to shifts in mode frequency or structure. The thermal enrichment of *para*-hydrogen has been known for 60 years. Optical pumping techniques have produced changes in the *ortho/para* varieties of Na_2^4, and evidence for nuclear polarization in cesium and rubidium dimers has been found in the form of nuclear magnetic resonance (NMR) signals in the respective optically pumped vapors.[13] Attempts to shift the *ortho/para* ratio in iodine have been shown to be inconclusive.[14] In the present case, the effect has been seen in a simultaneous measurement on several *ortho* and *para* rotational states in one experiment.

Light-induced shifts of reaction equilibria can be extended to other reactions, including heteronuclear systems and those other than the alkali metals. The effects of temperature, concentration, and buffer gas type may further elucidate the kinetic and mechanistic details.

In the past decade, considerable attention has been given to the possibility of using lasers to produce chemical changes that are significantly different from those obtainable with normal equilibrium or photochemical methods. The light-induced shift in chemical equilibria, such as described in this work, represents a unique approach to this problem with definitive results.

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