

Effects of atomic orientation on atom-dimer equilibria in alkali-metal vapors

R. J. Hoobler and R. A. Bernheim*

Department of Chemistry, Penn State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

(Received 19 September 1997)

Optical orientation of reagents is one approach to achieving selectivity in a chemical reaction and has been used successfully to shift the point of equilibrium in bulk reaction mixtures of alkali-metal atoms and dimers. In addition to the continuous control of the point of equilibrium in the dimerization of sodium atoms, the control of the ortho-para nuclear spin distribution is shown here to also be a function of the degree of atomic spin orientation over a broad range. The direction of the spin conversion is para to ortho. For a multicomponent vapor, the optical orientation of ${}^6\text{Li}$ in a mixture of lithium-6 and lithium-7 is shown to produce a continuous and selective control of the isotopic dimer concentrations. ${}^6\text{Li}_2$ (para) is selectively destroyed in the presence of the other dimer species. In this way the composition of a multicomponent metal vapor system at chemical equilibrium can be manipulated. The constraint produced by the optical orientation of one of the reagents offers a technique whereby the equilibrium yield of a multicomponent bulk chemical reaction can be laser controlled in a selective and continuous fashion. [S1050-2947(98)00203-0]

PACS number(s): 32.80.Bx, 34.50.Rk

I. INTRODUCTION

It is known that the point of equilibrium of a dimerization reaction $2A \leftrightarrow A_2$ can be shifted by optically orienting the angular momenta of the reagent atoms [1–7] and successful experiments have been conducted on dimerization reactions in several alkali-metal vapors. To achieve a chemistry in these systems that differs significantly from that which is statistically thermal, several conditions must be satisfied. First, the atomic orientation rates must be fast compared to the relaxation towards the thermal distribution. Second, the state into which the system is pumped must be strongly coupled to (or away from) the reaction pathway or potential-energy surface that is important for the reaction.

In a dilute spin-oriented alkali-metal atomic vapor, atoms collide with each other only along spin-triplet potential-energy surfaces correlating with the ${}^2S_{1/2} + {}^2S_{1/2}$ separated atomic ground states. This diatomic $a\ {}^3\Sigma_u^+$ potential is “antibonding,” having only a very weak dissociation energy compared to that of the more strongly bound $X\ {}^1\Sigma_g^+$ molecular ground state. For the normal thermal statistical distribution of atoms among their ground F, M_F states, collisions along both the $a\ {}^3\Sigma_u^+$ triplet antibonding and $X\ {}^1\Sigma_g^+$ singlet “bonding” trajectories take place. With the added presence of inert buffer gas atoms or molecules to provide the three-body collisions required to stabilize the formation of $X\ {}^1\Sigma_g^+$ molecules, the conditions of thermal dynamic equilibrium in the bulk mixture can be attained for the forward and reverse directions of the dimerization reaction. Atomic spin orientation produced by optical pumping results in an increase in the fraction of ${}^2S_{1/2} + {}^2S_{1/2}$ collisions that occur along the triplet, antibonding potentials and a decrease in the fraction along the singlet, bonding potentials. The atomic collisions are therefore directed away from the dimerization pathway producing a net decrease in dimer yield at equilibrium [8]. In

the absence of other rate processes or perturbations, complete spin orientation should stop the dimerization process. For conditions of reversibility, the position of the atom-dimer equilibrium will shift to eliminate the dimer component when the atoms are optically oriented. In real experiments on alkali-metal atom-dimer equilibria, measurement of the dimer density using laser-induced fluorescence (LIF) is a convenient and sensitive monitor of the point of equilibrium or yield of the reaction.

Previous work studying the effect of atomic orientation on the sodium atom-dimer equilibrium suggested that a simple, two-level model was sufficient to model the atom-dimer equilibrium in an oriented alkali-metal vapor [3,9]. However, it was also known that nuclear spin polarization and chemical exchange occur in optically oriented sodium vapor [10–14]. Recent work in our laboratory on the homonuclear alkali-metal vapors of lithium-6 and lithium-7 clearly demonstrated that nuclear spin cannot be neglected and a two-level model was inappropriate. In the case of lithium, the chemical exchange transfer of nuclear spin polarization process is very dramatic, leading to a large conversion of para to ortho molecules. With the experimental arrangement in the present work, it was possible to simultaneously probe many rotational states of the $\text{Na}_2\ A\ {}^2\Sigma_u^+ \leftarrow X\ {}^2\Sigma_g^+$ electronic transition and thus follow the ortho-para distribution as a function of atomic orientation. The present results on the effect of optical orientation of atomic sodium vapor show para to ortho conversion, but not to the extent found in lithium.

The results reported here on the mixed isotope system of lithium evolved from previous work in this laboratory on lithium-6 and lithium-7. As stated above, the para to ortho conversion that accompanies the orientation of atomic lithium is very dramatic, but initial studies of the mixed isotope system showed only a modest decrease in the ${}^6\text{Li}\ {}^7\text{Li}$ density [7]. However, the possibility of using laser radiation to selectively control a multicomponent system warranted further study. In the present experiments on the mixed isotope system of lithium, the molecular density of the five diatomic species present in the vapor could be simulta-

*Fax: (814) 865-3314. Electronic address: r5b@psu.edu

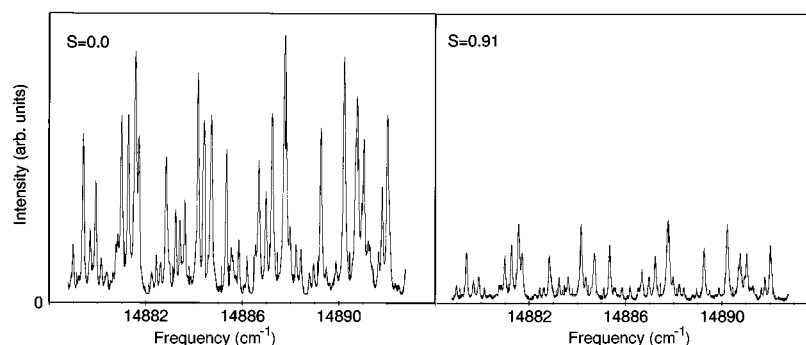


FIG. 1. Segment of the $^{23}\text{Na}_2$ LIF spectrum in sodium vapor at 548 K (left) in the absence of ^{23}Na atomic orientation and (right) with a ^{23}Na orientation of $S=0.91$.

neously monitored. The results show how one of these components in a lithium metal vapor mixture can be targeted to produce a change in the bulk equilibrium composition. These experiments clearly demonstrate some of the requirements necessary for laser control of a chemical reaction.

II. EXPERIMENT

The experimental arrangement has been described previously [5]. The atomic alkali-metal orientation is produced using the Dehmelt optical pumping configuration with circularly polarized D_1 radiation propagating parallel to an applied magnetic field [15]. The molecular density is monitored using LIF excited by a scanable single-mode ring dye laser (Coherent 899-29), the wavemeter of which was calibrated with the iodine spectrum. For both the sodium and the lithium experiments, the metal vapor was contained in 2-in.-I.D. stainless-steel cruciform heat-pipe cell placed in a 40-G magnetic field. The other experimental conditions are stated below.

III. RESULTS AND DISCUSSION

A. Sodium

The displacement of the sodium atom-dimer vapor equilibrium produced by atomic spin orientation is shown in Figs. 1 and 2 for the $2\text{Na} \leftrightarrow \text{Na}_2$ reaction where the decrease

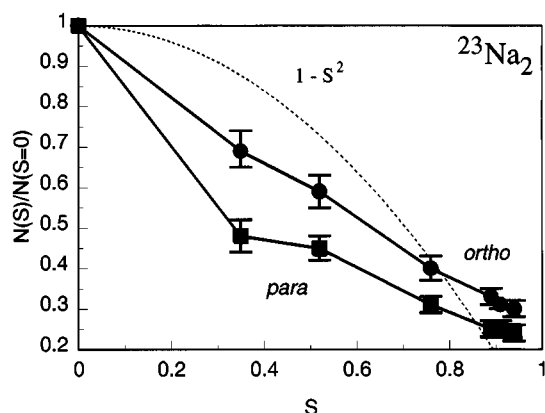


FIG. 2. Fractional change in molecular density for ortho- and para- Na_2 as a function of ^{23}Na atomic orientation. The $(1-S^2)$ dependence is that predicted from a two-level model for the $^2S_{1/2}$ ground electronic state of Na.

in the Na_2 density produced by optically orienting the atomic Na vapor component is clearly evident in the LIF spectrum of Na_2 . In this experiment a broadband multimode cw dye laser tuned to the $\text{Na}(3^2P_{1/2} - 3^2S_{1/2})$ resonance transition is used to optically orient the Na atoms while a single-mode cw ring dye laser is scanned across a segment of the $\text{Na}_2(A^1\Sigma_u^+ - X^1\Sigma_g^+)$ transition to monitor the Na_2 density. Variation of the optical pumping power is used to continuously control the degree of atomic orientation. For Na at 548 K and with 150 torr of Ne buffer gas, optical pumping powers up to 200 mW in a 1-cm-diam laser beam can be used before the onset of saturation of the resonance transition. The orientation parameter S is determined experimentally by measuring either the atomic fluorescence intensity or the transmitted circularly polarized optical pumping radiation [16]. Both approaches yield consistent values with $S=0$ designating no orientation and $S=1$ total orientation. Since ^{23}Na has nuclear spin, a fully relaxed distribution among the F, M_F hyperfine and Zeeman sublevels of the atomic ground state is indicated by $S=0$. Population of a single F, M_F level in the atomic ground state, where $|M_F|$ has its maximum value, corresponds to $S=1$. In Fig. 1 the 80% decrease in Na_2 density produced when the atomic orientation is changed from $S=0$ to near unity is dramatic.

Because $^{23}\text{Na}_2$ is a homonuclear diatomic molecule, its $X^1\Sigma_g^+$ ground-state rotational levels combine with nuclear spin functions determined by the particle statistics of the nuclei. As the ^{23}Na nuclei have spin $I = \frac{3}{2}$, they are fermions requiring the total molecular wave function to be antisymmetric with respect to an interchange of the nuclei. For the $X^1\Sigma_g^+$ ground electronic state (even symmetry) the ortho molecules (even nuclear spin symmetry) must belong to the molecular rotational states of odd J (odd symmetry), while the para molecules (odd nuclear spin symmetry) belong to states of even J . The concentrations of the ortho and para varieties of Na_2 can therefore be measured separately in the same experiment. The atomic M_F orientation and its accompanying nuclear spin polarization produced by the optical pumping are transferred to the nuclei of the dimer species resulting in a preference for ortho molecules at the expense of the para species. The nuclear spin polarization of the free alkali-metal dimers produced by transfer of orientation from optically pumped alkali atoms, observed [10,11] in Cs_2 and also [12] in Na_2 , is clearly evident in Fig. 2. The dependence of the Na_2 concentration as a function of atomic orientation S

is shown here for Na₂. For sodium vapor, the transfer of nuclear spin orientation from atoms to dimers was shown to take place primarily by a chemical exchange mechanism [13,14]. Here it is evident that the optical orientation of the Na atoms produces not only a continuously controlled change in the 2Na \leftrightarrow Na₂ atom-dimer chemical equilibrium composition of the vapor, but also the para \rightarrow ortho nuclear spin conversion for Na₂.

In the plot of molecular density expressed as $N(S)/N(S=0)$ vs S shown in Fig. 2, the LIF data are obtained from averages of the ($\nu'=\nu''=0$) transitions, $P(45)$, $P(44)$, $P(42)$, $R(49)$, $R(48)$, and $R(47)$, and from the ($\nu'=4; \nu''=0$) transitions, $P(33)$, $P(32)$, $R(38)$, $R(36)$, and $R(35)$. The experiment was repeated numerous times at each value of S with excellent reproducibility. The error bars show $\pm 1\sigma$.

For an atom-dimer reaction in which the atomic ground states have an idealized $M_s = \frac{1}{2}, -\frac{1}{2}$ two-level structure, a simple two-level model [9] results in an orientation dependence of the atom-dimer equilibrium constant for the optically oriented vapor system that changes as $K(S) = K(\text{thermal})(1 - S^2)$. Although the alkali-metal atoms with their hyperfine structure are clearly not two-level systems in their ground electronic states, this relationship has received some previous attention and predicts that the dimer density decreases with a $1 - S^2$ dependence on orientation [3,9]. As might be expected, the data in Fig. 2 deviates from this inappropriate model dependence for $2^{23}\text{Na} \leftrightarrow 2^{23}\text{Na}_2$. The fact that the Na₂ density is still significant at $S=0.94$ is due to competing relaxation processes such as collisional disorientation at the cell walls as well as continued evaporation from regions containing condensed metal. Nevertheless, the results show that the laser controlled equilibrium shift is clearly a substantial effect. When the orientation is forced to approach unity (complete orientation), the dimer density is reduced to 20% of its thermal value. A further decrease of Na₂ density may be possible by enlarging the vapor cell geometry to reduce wall relaxation, modifying the buffer gas composition and pressure, the use of wall coatings to further reduce wall relaxation, variation of the metal vapor density to change the metal-metal collision rates, change of temperature to change collision energies, etc. However, by showing the true dependence of the atom-dimer density and the dependence of the ortho-para distribution as a function of atomic orientation, the main objectives of the present experiment on sodium vapor have been achieved.

B. Lithium

A different objective is realized in an experiment on a 50%-50% mixture of lithium-6 and lithium-7 vapor. In this system, the continuous and selective control of the density of one of the many reaction products can be realized.

The role of nuclear spin symmetry has been explored [5-7] for ${}^6\text{Li}_2$, ${}^7\text{Li}_2$, and ${}^6\text{Li}{}^7\text{Li}$ where, for the homonuclear dimers, the ortho-para effects are clearly exhibited by the different nuclear spin statistics demanded by bosons ${}^6\text{Li}(I=1)$ and fermions ${}^7\text{Li}(I=\frac{3}{2})$. In separate experiments on pure ${}^7\text{Li}$ vapor and pure ${}^6\text{Li}$ vapor, the para variety was always found to be destroyed in preference to the ortho species. The ortho-para ratio can also be continuously controlled

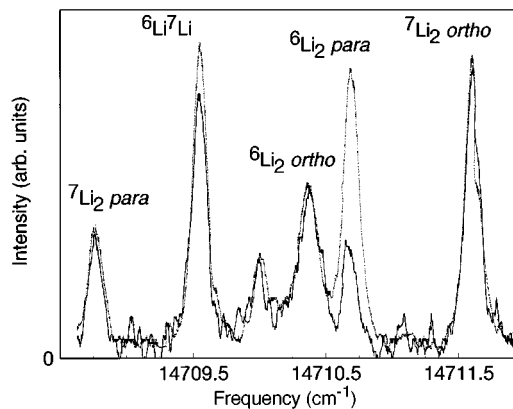


FIG. 3. Segment of the Li₂ LIF spectrum for a mixture of ${}^6\text{Li}_2$, ${}^7\text{Li}_2$, and ${}^6\text{Li}{}^7\text{Li}$ vapor at 783 K (.....) in the absence of ${}^6\text{Li}$ atomic orientation and (—) with a ${}^6\text{Li}$ orientation of $S=0.26$.

in these experiments on the separate isotopes of lithium. This means that in $2{}^6\text{Li} \leftrightarrow {}^6\text{Li}_2$ the shift in equilibrium away from dimers preferentially decreases the density of those ground-state ${}^6\text{Li}_2$ molecules that have odd values of the rotational quantum number J , while in the case of $2{}^7\text{Li} \leftrightarrow {}^7\text{Li}_2$ the shift preferentially decreases ${}^7\text{Li}_2$ with even J . In experiments on ${}^6\text{Li}{}^7\text{Li}$ there is no symmetry requirement and all rotational states of even and odd J are uniformly suppressed.

The mixed isotope system of ${}^6\text{Li}$ and ${}^7\text{Li}$ vapor provides an excellent opportunity to study the laser control of chemical equilibria in a more complex reaction mixture: ${}^6\text{Li}$, ${}^7\text{Li}$, ${}^6\text{Li}_2(\text{ortho})$, ${}^6\text{Li}_2(\text{para})$, ${}^7\text{Li}_2(\text{ortho})$, ${}^7\text{Li}_2(\text{para})$, and ${}^6\text{Li}{}^7\text{Li}$. Figure 3 shows a small segment of the lithium dimer LIF that exhibits spectral transitions for all five dimer species *simultaneously* and the resulting change when only one species, the ${}^6\text{Li}$ atoms, is optically oriented. This combined experiment differs from the previous studies where the three isotopic lithium dimers were studied in separate experiments, conducted at a time when two separate single-frequency lasers were not available in our laboratories. The line frequencies and assignments for the present work are given in Table I. The different feature of this series of experiments is the continuously controlled selective destruction of ${}^6\text{Li}_2(\text{para})$ in the presence of only a small decrease in equilibrium density of the other four dimer components in the reaction mixture as shown in Fig. 4. At first this result was surprising, but the selective behavior can be understood within the context of the various optical pumping, spin exchange, and relaxation rates that are responsible for the energy-level distributions of all participating reagents. As discussed below, it was anti-

TABLE I. A $1\Sigma_u^+ - X 1\Sigma_g^+$ dimer transitions in Fig. 5 monitored by LIF to measure the relative densities in the lithium mixed isotope vapor. NA denotes not applicable.

Vapor	(cm ⁻¹)	Assignment	Ortho or para
${}^7\text{Li}$	14 733.68	(4-0) $R(40)$	para
${}^6\text{Li}{}^7\text{Li}$	14 734.47	(4-0) $P(36)$	NA
${}^6\text{Li}_2$	14 735.29	(3-0) $R(22)$	ortho
${}^6\text{Li}_2$	14 735.61	(3-0) $P(17)$	para
${}^7\text{Li}_2$	14 736.53	(4-0) $P(35)$	ortho

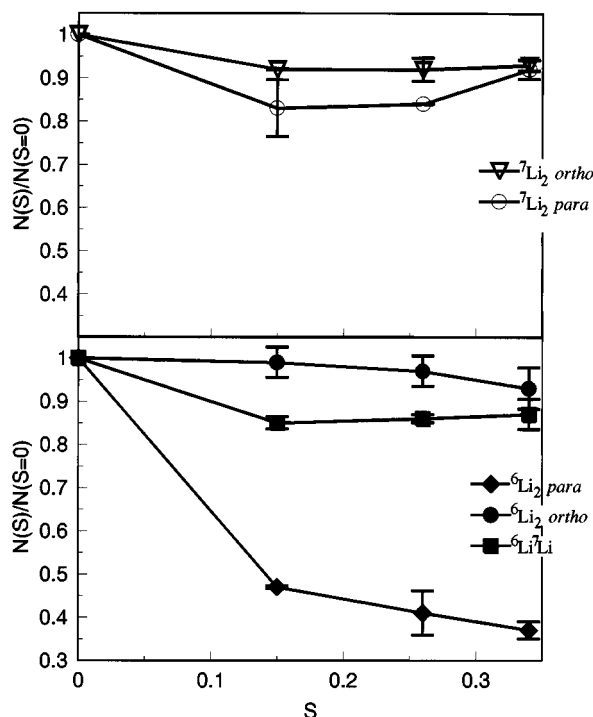


FIG. 4. Simultaneous fractional change in molecular density for ${}^6\text{Li}_2(\text{ortho})$, ${}^6\text{Li}_2(\text{para})$, ${}^7\text{Li}_2(\text{ortho})$, ${}^7\text{Li}_2(\text{para})$, and ${}^6\text{Li}{}^7\text{Li}$ as a function of ${}^6\text{Li}$ atomic orientation in a mixture of 50% lithium-6 and 50% lithium-7 vapor at 783 K. The data are separated into two plots to avoid congestion.

pated that optical pumping of ${}^6\text{Li}$ would have also resulted in an orientation of ${}^7\text{Li}$ through the electron spin exchange mechanism. An orientation of both ${}^6\text{Li}$ and ${}^7\text{Li}$ would produce a decrease of all dimer species accompanied by a para to ortho spin conversion for the two homonuclear components. However, under the present conditions, the transfer of orientation from ${}^6\text{Li}$ to ${}^7\text{Li}$ by spin exchange is inefficient and the chemical change is dominated by collisions between pairs of oriented ${}^6\text{Li}$ atoms and atomic exchange collisions of oriented ${}^6\text{Li}$ with ${}^6\text{Li}_2$. Furthermore, only a slight para to ortho conversion is observed for ${}^7\text{Li}_2$.

In the mixture, the selective optical orientation of ${}^6\text{Li}$ atoms is produced by single-mode circularly polarized D_1 radiation, ${}^6\text{Li}(3^2P_{1/2} \leftarrow 3^2S_{1/2})$, propagating parallel to the weak magnetic field. This atomic transition does not overlap any of those for ${}^7\text{Li}$, ensuring excitation only of ${}^6\text{Li}$. The experiment was carried out at temperatures between 680 and 800 K and with a He buffer gas pressure of 150 torr. The pump laser power required for the control of the optical orientation of ${}^6\text{Li}$ was varied up to a maximum of 30 mW in a 3-mm-diam beam, with saturation of the atomic pump transition again being one of the limiting factors for maximum atomic orientation. The frequency scanned probe laser beam used to detect Li_2 was 1 mm in diameter. The normal equilibrium metal vapor pressures at 783 K are [17] 5.1×10^{-3} torr for Li and 1.3×10^{-5} torr for Li_2 . It is possible to transfer some ${}^6\text{Li}$ orientation to ${}^7\text{Li}$ via electron exchange collisions provided the ${}^6\text{Li}$ and ${}^7\text{Li}$ atomic spin relaxation rates are significantly slower than the ${}^6\text{Li}$ - ${}^7\text{Li}$ spin exchange rate. For the experimental environment used here, the measured Li atomic spin relaxation time is 10^{-2} sec, which ap-

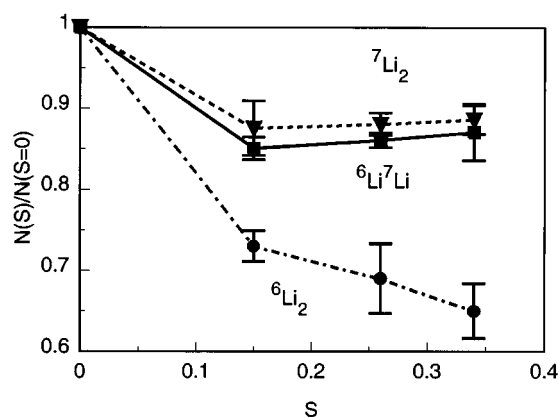
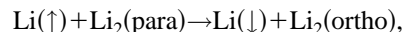


FIG. 5. Dependence of the average ${}^6\text{Li}_2$, ${}^7\text{Li}_2$, and ${}^6\text{Li}{}^7\text{Li}$ composition of a 50%-50% mixture of isotopes in the lithium vapor at 783 K as a function of ${}^6\text{Li}$ atomic orientation.

pears to be too fast to produce significant spin exchange. It is also one of the factors limiting the degree of ${}^6\text{Li}$ atomic orientation. While an accurate atomic Li spin exchange cross section is not yet available, the observations here indicate a negligible exchange transfer of orientation from ${}^6\text{Li}$ to ${}^7\text{Li}$. Additional support for this conclusion comes from the fact that optical radio-frequency double resonance experiments were not successful for the configuration where the ${}^6\text{Li}$ is optically pumped and the frequency is tuned to a ${}^7\text{Li}$ Zeeman resonance. Such spin exchange optically detected Zeeman resonances are easily observed in ${}^{85}\text{Rb}$ - ${}^{87}\text{Rb}$, where Rb spin relaxation times are typically in the range 0.5–1 sec or in mixtures of alkali-metal vapors where one species is optically pumped and the radio-frequency Zeeman transition of the other is probed, resulting in optical detection of the Zeeman resonance in the electronic transitions of the pumped species. The negligible transfer of orientation from ${}^6\text{Li}$ to ${}^7\text{Li}$ explains why the corresponding dimer densities for the $2\text{ }{}^7\text{Li} \leftrightarrow {}^7\text{Li}_2$ and ${}^6\text{Li} + {}^7\text{Li} \leftrightarrow {}^6\text{Li}{}^7\text{Li}$ reactions are only slightly affected by the ${}^6\text{Li}$ orientation. The selective destruction of ${}^6\text{Li}_2(\text{para})$ in the equilibrium mixture compared to ${}^6\text{Li}_2(\text{ortho})$ almost certainly arises from the chemical ex-



similar to the known mechanism for sodium vapor [13,14]. The disoriented $\text{Li}(\downarrow)$ product is subsequently optically reoriented and the elementary reaction step is repeated again and again until $\text{Li}_2(\text{para})$ has been converted to $\text{Li}_2(\text{ortho})$.

The overall chemical isotopic result is a decrease of ${}^6\text{Li}_2$ while ${}^7\text{Li}_2$ and ${}^6\text{Li}{}^7\text{Li}$ are substantially unchanged as shown in Fig. 5, where the nuclear spin symmetry species concentrations have been averaged for ${}^6\text{Li}_2$ and ${}^7\text{Li}_2$. The overall isotopic composition of the lithium dimers is thereby *manipulated* by means of the degree of ${}^6\text{Li}$ atomic orientation. The reproducibility of both the lithium and sodium experiments over many repetitions is indicated by the error bars, which are $\pm 1\sigma$.

The low orientation of ${}^7\text{Li}$ is responsible for the modest shift of the mixed isotope species ${}^6\text{Li}{}^7\text{Li}$ as well as ${}^7\text{Li}_2$. In order to reduce the spin relaxation rates several measurements were made for ${}^6\text{Li}{}^7\text{Li}$ at lower temperatures where a

TABLE II. Value of $N(S)/N(S=0)$ for ${}^6\text{Li } {}^7\text{Li}$ measured with several different rovibrational $A \ ^1\Sigma_u^+ - X \ ^1\Sigma_g^+$ transitions as a function of ${}^6\text{Li } D_1$ pumping power giving ${}^6\text{Li}$ atomic orientations to values of $S > 0.6$.

Transition ($v' - v''$)	S	Power (mW)	$N(S)/N(S=0)$	T (K)
(4-0) $R(34)$	0.62 ± 0.005	2.9	0.86 ± 0.012	680
	0.65 ± 0.014	5.3	0.91 ± 0.021	
	0.64 ± 0.025	14	0.88 ± 0.022	
	0.65 ± 0.034	30	0.80 ± 0.024	
(4-0) $R(34)$	0.19 ± 0.019	0.51	0.92 ± 0.014	700
	0.30 ± 0.013	1.0	0.84 ± 0.017	
	0.48 ± 0.008	28	0.84 ± 0.018	
(4-0) $R(33)$	0.19 ± 0.013	0.50	0.89 ± 0.004	700
	0.30 ± 0.019	1.0	0.86 ± 0.001	
	0.50 ± 0.018	27	0.90 ± 0.039	

higher orientation of ${}^6\text{Li}$ could be achieved. These results are given in Table II and show that even for relative high orientation ($S > 0.6$) the maximum decrease in ${}^6\text{Li } {}^7\text{Li}$ density is still only about 15%.

In a more general sense, these experiments are a clear demonstration of the conditions that must be fulfilled for laser control of a chemical reaction. One requirement is that the preparation rate of the optically pumped state be significantly greater than its relaxation rate to the other degrees of freedom available to the system. In the alkali-metal vapors there are a limited number of F, M_F states available to each atom, only one of which is populated by optical pumping at the expense of the others. At the same time, the spin relaxation or disorientation of the alkali-metal-atom ground states

can be targeted to a desired value through a choice of buffer gas pressure, cell dimensions, wall coatings, etc. A second requirement involves the relationship between the reaction pathway or potential-energy surface and the state that is optically pumped. In the present experiments, the optical orientation dictates that the atoms collide only on the spin-triplet antibonding surface. By placing the atoms on the potential-energy surface that does *not* connect with ground-state dimers the dimer yield is lowered and the dynamic equilibrium shifts to favor atoms.

As mentioned above, the degree of orientation S depends upon many factors such as the various relaxation mechanisms including disorientation collisions with the buffer gas and diffusion to the cell walls. In addition, the pumping laser bandwidth and power as well as the laser mode structure all affect the efficiency with which all velocity distributions of the alkali-metal atoms are optically pumped. If desired, these can be optimized for lithium by using a larger cell geometry, a different buffer gas and/or different buffer gas pressures, a laser linewidth more closely matched to the Doppler linewidth, etc. However, the main objective of the present study was to report the effect of optical orientation on a selected component of a complex reaction mixture. This study shows how the continuous control of the atomic orientation species can be used to control the chemical composition of the multicomponent vapor. With the mixed isotope lithium vapor, para ${}^6\text{Li}_2$ molecules are selectively destroyed, while a modest decrease in the other diatomic species is observed.

ACKNOWLEDGMENT

Support from the National Science Foundation is gratefully acknowledged.

-
- [1] G. Alzetta, A. Gozzini, and L. Moi, C. R. Acad. Sci. (Paris) B **274**, 39 (1972).
- [2] H. G. Weber and M. Stock, Phys. Lett. **50A**, 343 (1974).
- [3] M. Allegrini, P. Bicchi, and S. Gozzini, J. Chem. Phys. **82**, 457 (1985).
- [4] J. J. Ho, C. Wang, and R. A. Bernheim, J. Chem. Phys. **89**, 2635 (1988).
- [5] R. A. Bernheim, C. He, and G. Alzetta, J. Chem. Phys. **92**, 5959 (1990).
- [6] C. He and R. A. Bernheim, J. Chem. Phys. **95**, 8131 (1991).
- [7] C. He and R. A. Bernheim, J. Chem. Phys. **99**, 4215 (1993).
- [8] R. A. Bernheim, *Optical Pumping, An Introduction* (Benjamin, New York, 1965), p. 64.
- [9] A. Kastler, Acta Phys. Pol. **34**, 693 (1968).
- [10] H. Nienstädt, G. Schmidt, S. Ullrich, H. G. Weber, and G. zu Putlitz, Phys. Lett. **41A**, 249 (1972).
- [11] H. G. Weber, H.-J. Glas, R. Huber, M. Kompitsas, G. Schmidt, and G. zu Putlitz, Z. Phys. **268**, 91 (1974).
- [12] M. Kompitsas and H. G. Weber, Chem. Phys. Lett. **35**, 277 (1975).
- [13] R. Huber and H. G. Weber, Chem. Phys. **37**, 173 (1979).
- [14] H. G. Weber and R. Huber, Chem. Phys. **37**, 181 (1979).
- [15] H. Dehmelt, Phys. Rev. **105**, 1487 (1957).
- [16] See Ref. [5] for a description of the measurement of S .
- [17] Vapor pressures are obtained from M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed. (American Institute of Physics, New York, 1986).