

The 458 nm diffuse band of the lithium dimer

John T. Bahns, William C. Stwalley, and Goran Pichler

Citation: *The Journal of Chemical Physics* **90**, 2841 (1989); doi: 10.1063/1.455936

View online: <http://dx.doi.org/10.1063/1.455936>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/90/6?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Construction of narrow-band regenerative amplifier for momentum imaging spectroscopy of lithium dimer](#)

AIP Conf. Proc. **1465**, 58 (2012); 10.1063/1.4737540

[Study of the new 600.0nm diffuse band](#)

AIP Conf. Proc. **191**, 581 (1989); 10.1063/1.38635

[Direct excitation studies of the diffuse bands of alkali metal dimers](#)

J. Chem. Phys. **88**, 2235 (1988); 10.1063/1.454056

[Dissociative attachment to lithium dimers](#)

AIP Conf. Proc. **158**, 547 (1987); 10.1063/1.36574

[Infrared Spectra of the Lithium Halide Dimers](#)

J. Chem. Phys. **34**, 1071 (1961); 10.1063/1.1731650



The 458 nm diffuse band of the lithium dimer

John T. Bahns,^{a)} William C. Stwalley, and Goran Pichler^{b)}

Center for Laser Science and Engineering and Departments of Chemistry and Physics, University of Iowa,
Iowa City, Iowa 52242-1294

(Received 28 July 1988; accepted 25 November 1988)

Laser induced fluorescence studies of the lithium diffuse band at 458 nm were performed using single- and double-photon excitations. Single-photon excitation was performed using UV lines of Ar^{++} and Kr^{++} lasers, and the diffuse band fluorescence was induced by collisions in $^7\text{Li}_2$ and $^6\text{Li}_2$. The double-photon excitation process populated relevant upper states through several accidental coincidences for two-step excitation in $^7\text{Li}_2$. In two cases, in addition to structured continuum emission, an adjacent line spectrum was observed. In five other cases, two-photon accidental coincidences produced collision induced fluorescence of the $^7\text{Li}_2$ diffuse band. We also found (in a few cases) that the (two-photon) excitation energy of the $2^3\Pi_g$ state (with respect to the $1^3\Sigma_u^+$ state) was collisionally transferred to simultaneously excited lithium $2p$ atoms, thus creating a lithium atom in the $4d$ state.

I. INTRODUCTION

Several diffuse bands or structured continua of slightly different origin appear in the spectra of dense alkali vapors. They can be observed in absorption,¹ emission from electric discharge,² or laser induced fluorescence experiments.³ In this paper we shall discuss the case of the lithium dimer diffuse band at 458 nm connected with the spectral transition from the $2^3\Pi_g$ electronic state to the $1^3\Sigma_u^+$ state (the lowest triplet state, having a very shallow potential well). This diffuse band appears quite peculiar in nature because of several extraordinary features, which for a long time have puzzled many researchers. The relatively large intensity and interesting shape of the 458 nm diffuse band are connected with the rapid increase of the transition dipole moment towards smaller internuclear separations and with the existence of two extrema in the relevant difference potential curve.⁴ The case of the lithium diatomic molecule is attractive since it is one of the simplest dimer molecules and in many aspects is similar to the hydrogen molecule, but with its strongest and most interesting bands in the visible spectrum.

Recently, the 458 nm lithium dimer diffuse band was discussed as a special case of other alkali diffuse bands connected with the triplet electronic states,⁵ and a qualitative interpretation was given by means of the relevant theoretical potential curves.⁶ The corresponding measurements were performed in absorption where the overlap with the $\text{Li}_2 B-X$ molecular band was a serious hindrance for the observation of the main diffuse band peak. This obstacle was overcome by using UV Ar^{++} laser lines, which induced weak fluorescence at about 455 nm in a diffuse band.⁷ This mode of excitation is well known in all other alkali dimer cases.⁸ It is thought to involve single-photon absorption followed by collisional energy transfer to the $2^3\Pi_g$ state. In the present experiment, we used all available UV lines of Ar^{++} and Kr^{++} lasers in order to selectively pump the $C^1\Pi_u$ electronic state of Li_2 .

Another mode of excitation is two-photon absorption. In this way a single rotational-vibrational level of the $2^3\Pi_g$ state may be prepared, due to the mixing between $A^1\Sigma_u^+$ and $b^3\Pi_u$ electronic states.⁹ Such mixed levels serve as intermediate levels in this excitation scheme. Quite recently,¹⁰⁻¹² it was shown that such mixing, although of smaller magnitude than in the heavier alkalis, exists even in the case of a lithium dimer molecule. In fact, Field and co-workers¹³⁻¹⁵ used this scheme (perturbation facilitated optical-optical double resonance, PFOODR) to reach several excited triplet states by two-photon absorption from the singlet ground state of $^6\text{Li}_2$.¹³ They used a very few perturbed intermediate levels that were not affected by the accidental predissociation by the $1^3\Sigma_u^+$ state of the $b^3\Pi_u$ state.^{11,12} A very precise analysis for $^6\text{Li}_2$ of the lowest¹⁴ and some of the excited electronic states¹⁵ now presents a solid foundation for further refinements of theoretical calculations and possible laser and spectroscopic applications. In addition to this highly selective excitation mechanism, there is another possibility: excitation of the diffuse band fluorescence by tuning the laser to the center¹⁶ or to the self-broadened¹⁷ wings of the first resonance lines. Both of these two-photon excitation processes have been investigated in the present experiment with the use of a DCM dye laser for the excitation of metal vapor.

All of the abovementioned excitation mechanisms are of considerable importance in connection with possible realization of tunable laser action at the excimer transitions corresponding to the diffuse band emission.¹⁸

In the next section, we shall describe the experimental apparatus with some details of the experimental procedure. In Sec. III, we present the results of the one-photon and the two-photon laser induced fluorescence experiments on the Li_2 molecule, using arguments based on recent theoretical calculations.^{19,20} In addition to this, a proposed collision mechanism between an excited Li_2 molecule and an excited Li atom is discussed.

II. EXPERIMENT

Laser induced fluorescence spectra have been obtained by using several lasers, a conventional crossed heat pipe oven and a scanning monochromator, followed by a detection sys-

^{a)} Present address: Pacific Sierra Research, 12340 Santa Monica Boulevard, Los Angeles, California 90025.

^{b)} Permanent address: Institute of Physics of the University, P. O. Box 304, 41001 Zagreb, Yugoslavia.

tem and recording devices. For single-photon excitation, we used the UV lines from Ar^{++} and Kr^{++} lasers (Coherent CR-18 UV and 3000 K) and for two-photon excitation we used the multimode output from a cw dye laser (Coherent 599) operating with DCM dye. The UV laser lines were spatially separated by means of a Pellin-Broca quartz prism. We could operate argon and krypton UV laser lines over a gain bandwidth of $\sim 2\text{--}6$ GHz in a single longitudinal mode by means of an intracavity Fabry-Perot etalon. Different longitudinal modes could be generated simply by tilting the etalon. Within the gain profile of these UV laser lines, we did not observe significant differences in the fluorescence spectra. This can be understood by considering the large Doppler width (~ 2 GHz) of each molecular absorption line and the relatively sparse nature of the Li_2 spectra compared to heavier dimers. Continuous scanning of the multimode output from the DCM dye laser was performed by rotating a birefringent filter.

The heat pipe oven used in the present experiment had a special design utilizing a horizontal cross and one vertical arm, through which a thermocouple was inserted for the direct temperature measurement slightly above the illuminated vapor. Helium was used as a buffer gas in the range of pressure from 1 to 6 Torr. The temperature was varied from 660 to 770 °C. At the typical temperature of 700 °C, the estimated pressure of lithium atoms was 0.42 Torr, and the corresponding pressure of lithium molecules was 0.012 Torr. Thus, the oven was not operating in a true heat pipe regime (i.e., $P_{\text{He}} \gg P_{\text{Li}} + P_{\text{Li}_2}$). A system of mirrors and lenses was used to direct and focus the laser beam in the middle of the heat pipe oven cross. The fluorescence of the metal vapor was recorded at a right angle by means of a scanning monochromator with moderate resolution (Jarrell-Ash 0.5 m). Spectrally resolved light at the exit slit was detected by a channeltron photomultiplier (Bendix BX 754, S20). The signal (with a low dark current background) was sent to a strip chart recorder after appropriate amplification. The accuracy of the spectral position measurements was about 0.05 nm.

Once the diffuse band of the lithium dimer molecule was found, the monochromator was set at the position of the main peak close to 458.5 nm. Then the wavelength of either the UV lines or the DCM dye laser lines was changed in order to find single-photon or two-photon absorption resonances, respectively.

III. RESULTS

A. Single-photon excitation with UV ion laser lines

Ultraviolet lines of argon and krypton ion lasers have been used to excite the $C^1\Pi_u \leftarrow X^1\Sigma_g^+$ absorption of $^6\text{Li}_2$ and $^7\text{Li}_2$. In addition to the observed $C \rightarrow X$ fluorescence, collision-induced molecular emissions have also been observed: (1) Diffuse band emission near 458 nm ($2^3\Pi_g \rightarrow 1^3\Sigma_u^+$); (2) bound-bound emission to the $b^3\Pi_u$ state in the 500–630 nm range. The experiments (carried out in the helium pressure range 1–6 Torr and temperature range 660–770 °C) are summarized in Table I and an example is given in Fig. 1. Note that many lines do not populate the $C^1\Pi_u$ state and therefore do not produce collision-in-

TABLE I. Summary of collision-induced triplet emission in $^6\text{Li}_2$ and $^7\text{Li}_2$ excited by UV ion laser lines.

Molecule	λ_{EXC} (nm)	$C^1\Pi_u \leftarrow X^1\Sigma_g^+$ Excitation $v'', J'' \rightarrow v', J'$	λ_{EM} (nm)	
			$2^3\Pi_g \rightarrow 1^3\Sigma_u^+$ Peak	$3^3\Pi_u \rightarrow b^3\Pi_u$ Range
$^6\text{Li}_2$	324.0	a
	333.6	a
	334.5	a
	335.8	a
	337.5	a
	350.7	a
	351.1	7,12 \rightarrow 2,12 ^b	458.0	500–600
	351.4	... ^b	...	a
	356.4	a
	363.8	... ^b	...	a
$^7\text{Li}_2$	324.0 ^c	0,53 \rightarrow 4,54	456.5	520–630
	333.6	3,35 \rightarrow 3,36 ^d	458.5	a
	334.5	1,77 \rightarrow 4,77 ^d	458.5	504–600
	335.8	a
	337.5	4,34 \rightarrow 3,34	458.5	a
	350.7	a
	351.1	4,67 \rightarrow 0,66 ^b	458.0	504–600
	351.4	... ^b	...	a
	356.4	a
	363.8	... ^b	...	a

^a Not investigated.

^b Reference 21.

^c Shown in Fig. 1.

^d Tentative.

duced emission. In addition, it is worth noting that shorter wavelength exciting lines usually involved transitions from lower v'' and produce excitation of higher v' . If J values and Franck-Condon factors are comparable, lower v'' (shorter wavelength) suggests stronger excitation and emission; although we have not attempted to study this quantitatively, the 324.0 nm excitation of $^7\text{Li}_2$ appeared to give the strongest emission. Likewise, higher v' suggests a broader range of

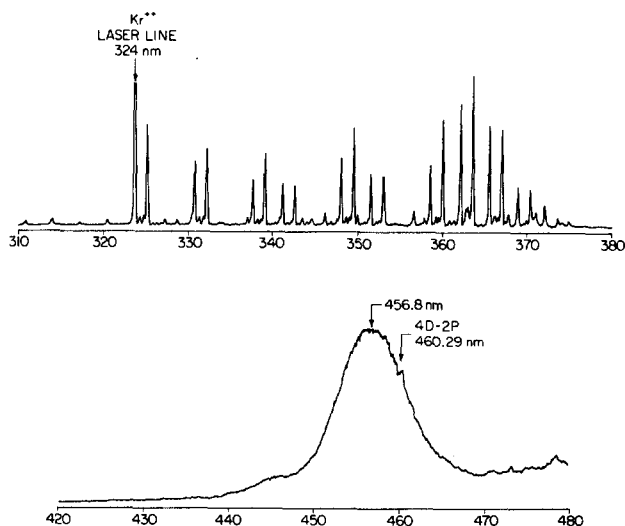


FIG. 1. The $^7\text{Li}_2$ fluorescence spectrum excited by the UV Kr^{++} 324 nm laser line. There is no significant emission in the 380–420 nm region. The 420–480 nm region is on a scale three times less sensitive than the 310–380 nm region.

emission wavelengths. Again, the 324.0 nm excitation of ${}^7\text{Li}_2$ (the shortest wavelength) gave the broadest collision-induced bound-bound emission and exhibited the shortest wavelength diffuse band emission peak (456.5 vs 458.0–458.5 nm) and broadest width [full width at half-maximum (FWHM) ~ 9.5 vs ~ 8 nm in other cases]. The weak diffuse band shoulder near 446 nm also shifted slightly, appearing at 445 nm with 324.0 nm excitation and at 446.5 nm with 337.5 nm excitation. Finally, it should be noted that the 324.0 nm laser line is close to the $\text{Li}(2s \rightarrow 3p)$ excitation at 323.3 nm; thus some contribution to the observed emission may arise from atomic rather than molecular excitation.

The collision-induced bound-bound emission in the 500–630 nm region should include $2\,{}^3\Pi_g \rightarrow b\,{}^3\Pi_u$ diffuse emission (since the $2\,{}^3\Pi_g$ is populated to produce the diffuse band emission). However, collision-induced $1\,{}^3\Delta_g \rightarrow 1\,{}^3\Sigma_u^+$ emission has also been observed in this region.⁷ Since $1\,{}^3\Delta_g \rightarrow 1\,{}^3\Sigma_u^+$ is forbidden, it is likely that the branching ratio for 500–630 nm emission versus total emission is much greater for this $1\,{}^3\Delta_g$ state than for the $2\,{}^3\Pi_g$ state. In addition, the possibility of 500–630 nm emission from the $3\,{}^3\Sigma_g^+$ state is not excluded here. The two-photon excitation results presented in the next subsection include many examples where strong diffuse band emission is seen without significant 500–630 nm emission, suggesting that $2\,{}^3\Pi_g \rightarrow b\,{}^3\Pi_u$ emission is at most a minor component of the 500–630 nm emission seen here.

B. Two-photon excitation

Originally the main purpose of the two-photon excitation experiment was to test whether two photons of equal energies, tuned over the self-broadened wings of the lithium resonance line at 670.8 nm, produce ${}^7\text{Li}_2$ diffuse band fluorescence in the blue region of the visible spectrum. Similar experiments have been performed in the case of Na_2 and K_2 .^{16,17} We expected some important differences in the case of lithium dimer two-photon excitation, due to much smaller (but still not negligible) spin-orbit interaction within $2p + 2s$ asymptote (see Table II).

We find that, unlike the Na_2 and K_2 cases, no continuous enhancement of the ${}^7\text{Li}_2$ diffuse band fluorescence was observed when the DCM dye laser was continuously tuned over the region of the self-broadened wings of the Li resonance line at 670.8 nm. Quite on the contrary, we have thus far found seven discrete dye laser wavelengths, at 677.05, 671.9, 671.75, 669.9, 669.6, 668.7, and 662.15 nm, which excited the fluorescence of the blue diffuse band peaking at about 458 nm. We have determined that this fluorescence was quadratically dependent on the input dye laser intensity in all seven cases. In five cases, the laser excitation lines at 662.15, 668.7, 669.6, 669.9, and 671.75 nm induced a very weak fluorescence of the diffuse band at ~ 458 nm, with no oscillatory continuum structure. In one of these cases, the excitation line at 668.7 nm also produced the bound-bound triplet transitions ($1\,{}^3\Delta_g, 2\,{}^3\Pi_g, 3\,{}^3\Sigma_g^+ \rightarrow b\,{}^3\Pi_u$) in the spectral interval from 465 to about 600 nm.

In Fig. 2 we present the sixth case where the dye laser was set at about 677.05 nm. The fluorescence intensity shape consists of continuous oscillations, of which one (at 458.5 nm) is especially enhanced. Two sharply peaked regions ap-

TABLE II. Two-photon ${}^7\text{Li}_2$ excitation results: dye laser wavelengths near the $\text{Li}(2s \rightarrow 2p)$ resonance line at 670.8 nm resulting in 458 nm diffuse band emission.

Dye laser λ (nm, air) ^a	Oscillatory structure for $\lambda < 458$ nm	${}^3\Lambda_g \rightarrow b\,{}^3\Pi_u$ (465–600 nm)	Enhancement of 460.2 nm Li line
677.05 ^b	Y	Y	N
671.9 ^c	Y	N	N
671.75	N	N	Y
669.9	N	N	Y
669.6	N	N	Y
668.7	N	Y	Y
662.15	N	N	N

^aUncertainty ± 0.05 nm.

^bSee Fig. 2.

^cSee Figs. 3(a) and 3(b).

pear at the short wavelength end of these oscillations, close to 440 nm. The very pronounced peak at 458.5 nm, the oscillatory continuum structure and the two sharply peaked regions at the short wavelength end suggest that in this case the laser line at 677.05 nm excited a single rotational-vibrational level in the $2\,{}^3\Pi_g$ state. The strong peak is caused by the existence of the minimum in the relevant difference potential curve with the $1\,{}^3\Sigma_u^+$ state. As can be seen from Ref. 20, the $2\,{}^3\Sigma_g^+ - 1\,{}^3\Sigma_u^+$ difference potential has no extremum and there will be no enhancement comparable to the case of the minimum in the $2\,{}^3\Pi_g - 1\,{}^3\Sigma_u^+$ difference potential. On the longer wavelength side of the strong peak at 458.5 nm, relatively weak discrete molecular lines from the ${}^3\Lambda_g \rightarrow b\,{}^3\Pi_u$ transitions (see Sec. III A above) could be observed up to about 570 nm, where they started to blend with anti-Stokes lines from the $A\,{}^1\Sigma_u^+ - X\,{}^1\Sigma_g^+$ laser induced fluorescence spectrum.

The final case, excited by two photons at 671.9 nm, and shown in Fig. 3(a), consists of more sharply peaked features for $\lambda < 458.5$ nm, which approach the shifted diffuse band maximum at 460 nm. At wavelengths longer than 458.5 nm, the diffuse band has a purely continuous appearance. It seems as though the main maximum of the otherwise continuous diffuse band was split into two parts, sharply peaked features and an adjacent smooth continuum. In this case, we

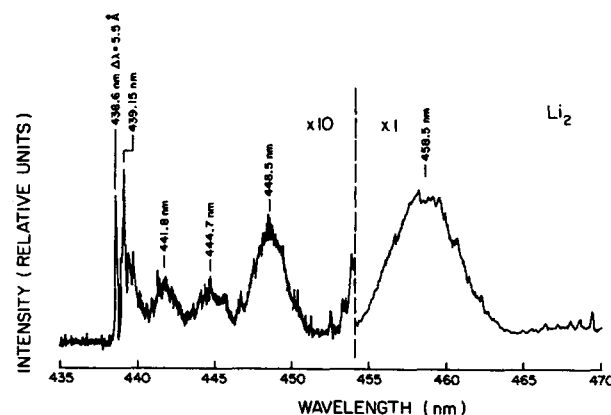


FIG. 2. The ${}^7\text{Li}_2$ fluorescence spectrum excited by a two-photon transition at 677.05 nm.

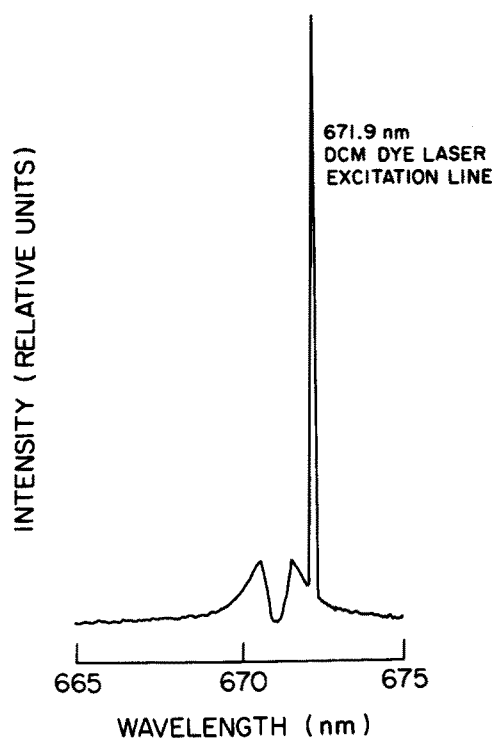
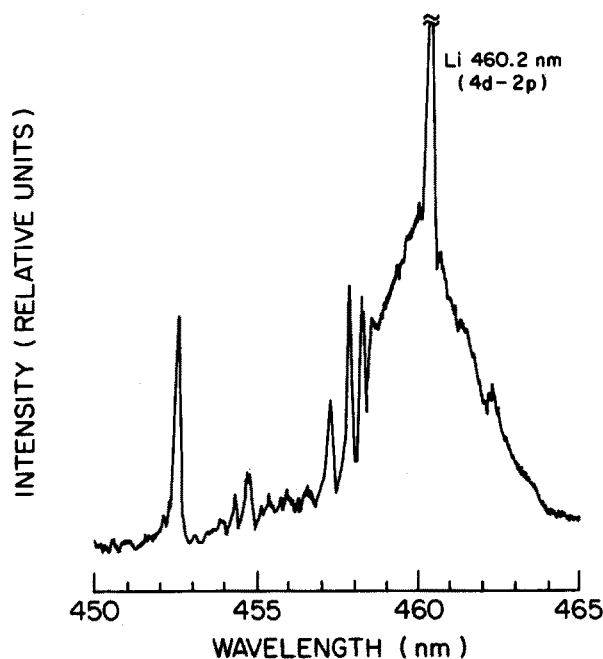


FIG. 3. (a) The ${}^7\text{Li}_2$ fluorescence spectrum of the blue diffuse band excited by a two-photon transition at 671.9 nm. The atomic line at 460.2 nm is twice as intense as the adjacent continuum. (b) The fluorescence of the lithium resonance line in the immediate neighborhood of the laser line at 671.9 nm. The dip at the center of the resonance line is caused by the reabsorption of the resonance radiation.

have observed an extraordinary enhancement of the lithium atomic line at 460.2 nm corresponding to the $4d \rightarrow 2p$ transition. The fluorescence spectrum in the immediate neighborhood of the lithium first resonance line, centered at 670.8 nm, is shown in Fig. 3(b). It can be seen that the laser line at 671.9 nm efficiently excited the fluorescence of the symmet-

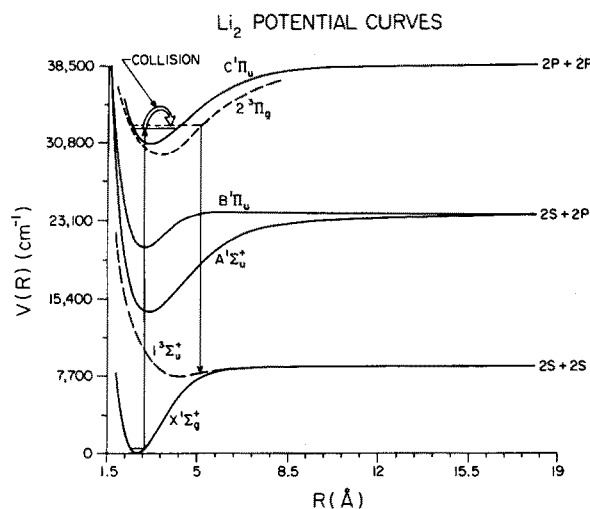


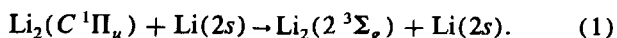
FIG. 4. Excitation scheme for the one-photon excitation followed by the collisional energy transfer.

ric wings of the self-broadened lithium resonance line. The line center is strongly influenced by the absorption of resonance radiation along the observation direction. In this case, the laser simultaneously excited lithium atoms to the $2p$ resonance level. We have checked the fluorescence intensity dependence of the atomic line at 460.2 nm and one of the sharply peaked features at shorter wavelength. The sharply peaked feature exhibited a quadratic dependence on the dye laser intensity, while the atomic line at 460.2 nm had a cubic dependence. This experiment was performed using appropriate neutral density filters, which were placed in front of the entrance window of the heat pipe oven. Similar behavior has been found in four other accidental coincidences at 668.7, 669.6, 669.9, and 671.75 nm. In all these cases the collision induced diffuse band was observed with the enhancement of the atomic lithium line at 460.2 nm. In the case of the laser line at 669.9 nm, the atomic line was about 14 times stronger than the continuum of the diffuse band underneath. The enhancement of the atomic line was stronger the closer the excitation laser line was to the center of the lithium resonance line at 670.78 nm, although only when sufficiently far out on its wings to be unaffected by the reabsorption of the resonance radiation. It is interesting that sharply peaked features in Fig. 3(a) come up almost exactly to the 458.5 nm peak, where the maximum of the blue diffuse band usually occurs. The whole appearance of the diffuse band seems to be slightly shifted towards longer wavelengths because of the enhancement of the atomic line at 460.2 nm. The separation of the shortest wavelength sharply peaked feature and the location where the continuous diffuse band changes into discrete molecular lines is about 290 cm^{-1} .

IV. DISCUSSION

A. Excitation by a single photon

The excitation scheme suggested for the description of the single UV photon process is shown in Fig. 4. The appropriate laser photon first excites a certain rotational-vibrational level in the Li_2 $C\ ^1\Pi_u$ state. Then energy transfer takes place by collisions with ground-state lithium (or helium) atoms as follows:



The cross section for this collisional energy transfer certainly depends on the separation between rotational-vibrational levels in these two electronically excited states. From the observed shape of the blue diffuse band shown in Fig. 1, it can be inferred that more than one rotation-vibration level in the $2^3\Sigma_g^+$ state is collisionally populated. The fluorescence from this group of levels to the lowest triplet electronic state ($1^3\Sigma_u^+$) results in a continuous diffuse band, as shown in Fig. 1.

It would be interesting to measure the variation of the cross section for the collision energy transfer process in Eq. (1) by varying the excitation energy in the C state. Such a study might suggest possible ways of obtaining population inversion and lasing within the blue diffuse band of the lithium dimer.¹⁸

B. Excitation by two photons

In order to explain the two-photon excitation process, we present in Fig. 5 the relevant energy curves taken from the recent calculations by Konowalow and Fish.¹⁹ Essentially this is an optical-optical double resonance excitation process which connects the $X^1\Sigma_g^+$ state with the $2^3\Pi_g$ state by means of intermediate levels of mixed $A^1\Sigma_u^+$ and $b^3\Pi_u$ character. The OODR excitation scheme has been successfully used in the Na_2 case²² due to the relatively large spin-orbit coupling constant. In the case of Li_2 , the relevant spin-orbit interaction is so small that until recently¹⁰⁻¹² one did not expect an observable perturbation between the A and b

electronic states.²³ Preuss and Baumgartner²⁴ have found 33 perturbed levels in $^7\text{Li}_2$, 28 in $^6\text{Li}_2$, and 24 in $^6\text{Li}^7\text{Li}$. Field *et al.*¹³⁻¹⁵ have used several states of mixed A - b character which do not predissociate for their PROODR in $^6\text{Li}_2$. We assume that we have found similar perturbed levels in the present experiment for $^7\text{Li}_2$. Because of energetics, all these levels should correspond to lower vibrational levels in the $A^1\Sigma_u^+$ state. It can be inferred from Fig. 5 that in this region the A and b states cross, which certainly enhances the magnitude of perturbation. It is interesting that in our two-photon excitation process, both photons have the same energy. Therefore, we feel we have found accidental coincidences in the present experiments by tuning the dye laser and observing fluorescence in the blue region. It is also obvious that in the two cases shown in Figs. 2 and 3 we have excited very low vibrational levels in the $2^3\Pi_g$ state. In Fig. 6 we present the $1^3\Sigma_u^+$ state with a family of Mulliken difference potential curves^{25,26} corresponding to several chosen vibrational levels in the $2^3\Pi_g$ state. We conclude that the fluorescence spectrum shown in Fig. 2 is probably produced by excitation to a vibrational level with v' in between five and ten, since in this case the relevant rotationless Mulliken difference potential does drop below the dissociation limit, thus sampling two regions of discrete molecular transitions, the sharply peaked features at 438.6 and 439.15 nm.

The spectrum shown in Fig. 3(a) can be produced by exciting the $2^3\Pi_g$ state into $v' = 2$, since in this case the maximum of the relevant Mulliken difference potential lies only slightly above the dissociation limit of the $1^3\Sigma_u^+$ state. The part of the Mulliken difference potential that samples levels in the continuum of the lower electronic state is responsible for the continuous part of the observed diffuse band in Fig. 3(a). The sharply peaked features observed in Fig. 3(a) have a peculiar envelope since the corresponding Mulliken difference potential samples bound levels in the $1^3\Sigma_u^+$ state at two Condon points, the amplitudes of which may constructively or destructively interfere. We may estimate that this "discrete part" of the diffuse band spans a

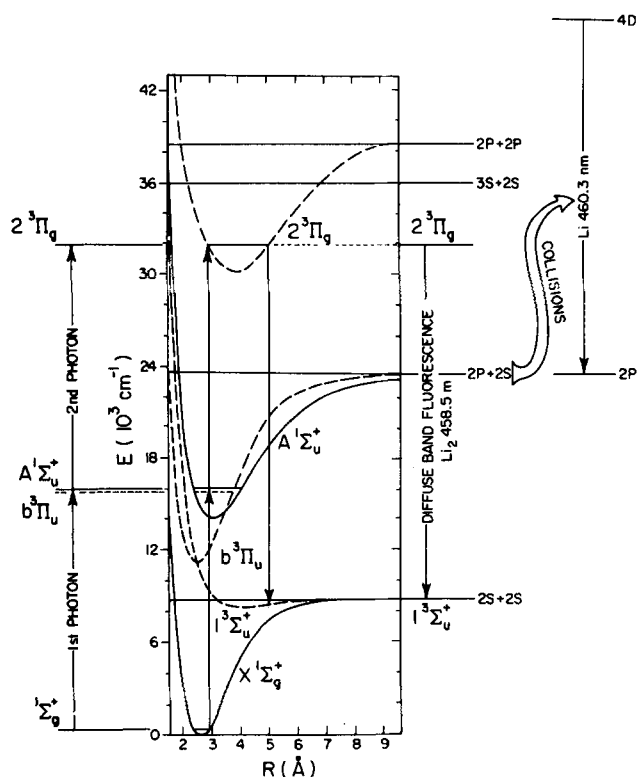


FIG. 5. Excitation scheme for the two-photon excitation of single rotation-vibration levels. On the right-hand side of the figure, the collisional energy transfer process (4) is schematically shown.

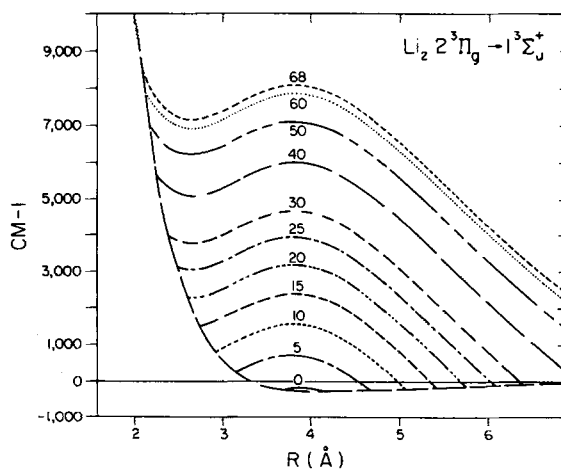


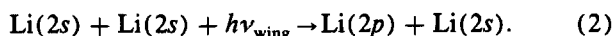
FIG. 6. The family of Mulliken difference potential curves (MDPs) between the $2^3\Pi_g$ and $1^3\Sigma_u^+$ states, for the selected vibrational levels of the $2^3\Pi_g$ state (for $J = 0$). The molecular constants for the $2^3\Pi_g$ state have been calculated from the potential curve of Ref. 19. The potential curve of the $1^3\Sigma_u^+$ state was taken from the same reference.

region of about 290 cm^{-1} . This value compares well with the accurate spectroscopic value¹⁴ for D_0 of 298.5 cm^{-1} .

It would be desirable, in the future, to use experimental or theoretical potential curves and transition moments to calculate spectral simulations in cases such as those presented in Figs. 2 and 3(a).

C. The enhancement of atomic Li line at 460.2 nm

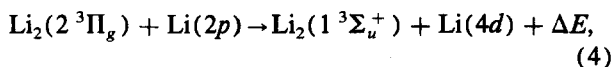
We have found five accidental coincidences in the present optical-optical double resonance excitation of the $2^3\Pi_g$ state, at which a strong enhancement of the lithium atomic line at 460.2 nm has been observed. This enhancement was observable only when the vapor pressure was sufficient for the single-photon excitation of the lithium atom into the $2p$ state, by means of the line wing absorption:



Furthermore, the Li 460.2 nm line and the blue diffuse band of Li_2 overlap in the spectrum, which means that

$$[E(4d) - E(2p)] \simeq [E(2^3\Pi_g) - E(1^3\Sigma_u^+)]. \quad (3)$$

This suggests that the following collision-induced energy transfer takes place for the abovementioned five accidental coincidences:



where ΔE is less than 100 cm^{-1} . This process is schematically shown in Fig. 5. The excitation energy of the $2^3\Pi_g$ state (compared to the ground-state asymptote) is transferred to an already excited lithium atom (in the $2p$ state), thus creating a lithium atom in the $4d$ level. From Eq. (4), it immediately follows that the fluorescence of the atomic line at 460.2 nm will depend on the cube of the dye laser intensity, as was confirmed in the present experiment. The fluorescence of this atomic line means repopulation of the lithium atoms into the $2p$ level, which may again be involved in the process (4). It is interesting to note that both incoming particles in (4) are in their excited states. The collisional process (4) should be allowed according to long-range dipole-dipole interactions.²⁷ The cross section could be appreciable since the corresponding optical transition dipoles, which connect two molecular and two atomic states, are relatively large.

V. CONCLUSION

In conclusion we note that the present study has established the location in the spectrum of the blue diffuse band of the lithium dimer molecule, by means of single-photon excitation, followed by collision induced fluorescence measurements. Two-photon excitation studies have revealed the existence of several accidental coincidences which were used for the population of the upper electronic state ($2^3\Pi_g$) responsible for the formation of the diffuse band in $^7\text{Li}_2$. In addition to bound-free emission, bound-bound lines have been observed in the case of two such accidental coincidences, from which the lower bound for the dissociation energy of the $1^3\Sigma_u^+$ state has been estimated to be 290 cm^{-1} . Whenever the accidental coincidences simultaneously excited lithium atoms into the $2p$ state, we observed appreciable

enhancement at the atomic $4d \rightarrow 2p$ transition. This was interpreted in terms of the collision-induced energy transfer process (4), in which both Li_2 and Li enter as excited species. It would be interesting to study the reverse process in Eq. (4) [or $2\text{Li} + \text{Li}(4d) \rightarrow \text{Li}_2(2^3\Pi_g) + \text{Li}(2p)$], which might explain the appearance of the diffuse band of alkali dimers in plasmas created by either resonance, quasiresonance or two-photon laser irradiation²⁸ or by negative corona discharge.²⁹

We intend to further study the $^7\text{Li}_2$ triplet state manifold ($1^3\Sigma_u^+$, $2^3\Pi_g$, $3^3\Sigma_g^+$, $1^3\Delta_g$, $b^3\Pi_u$) using accidental coincidences (via levels of mixed $A^1\Sigma_u^+ - b^3\Pi_u$ character) found in the present work at 671.9 and 677.05 nm by means of the single mode-single frequency excitation PFOODR scheme as employed by Field and co-workers.¹³⁻¹⁵

It is strange that $2p \rightarrow 3d$ quasiresonant excitation³⁰ produces blue diffuse band emission from the $2^3\Pi_g$ state while $2s \rightarrow 2p$ resonant excitation, leading to $\text{Li}(2p) - \text{Li}(2p)$ collisions, apparently does not produce such emission. Perhaps $2p-2p$ collisions produce $3^3\Pi_g$ or $4^3\Pi_g$ states diabatically while $3d-2s$ collisions produce the $2^3\Pi_g$ state diabatically (see the discussion of Xie and Field¹⁵).

ACKNOWLEDGMENTS

One of us (G.P.) would like to express his gratitude for the hospitality shown to him during his stay in the Iowa Center for Laser Science and Engineering. We also thank G. Baumgartner, W. Preuss, and R. W. Field for helpful discussions. Help and encouragement from Li Li and M. Lyyra are also gratefully acknowledged. This work was supported in part by the National Science Foundation and the Air Force Office of Scientific Research.

¹R. Gupta, W. Happer, J. Wagner, and E. Wennmyr, *J. Chem. Phys.* **68**, 799 (1978); R. Beuc, S. Milosevic, and G. Pichler, *J. Phys. B* **17**, 739 (1984); J. M. Walter and S. Barrat, *Proc. R. Soc.* **119**, 257 (1928).

²H. Bartels, *Z. Phys.* **73**, 203 (1932); M. M. Rebbeck and J. M. Vaughan, *J. Phys. B* **4**, 258 (1971); Yu. P. Korchevoi, V. I. Lukashenko, and S. L. Lukashenko, *Phys. Scr.* **19**, 271 (1979).

³J. P. Woerdman, *Chem. Phys. Lett.* **43**, 279 (1976); *Opt. Commun.* **26**, 216 (1978); M. Allegrini and L. Moi, *ibid.* **32**, 91 (1980); C. Radzewicz, P. Kowalczyk, and J. Krasinski, *Z. Phys. A* **314**, 293 (1983).

⁴D. D. Konowalow, S. Milosevic, and G. Pichler, *J. Mol. Spectrosc.* **110**, 256 (1985).

⁵G. Pichler, S. Milosevic, D. Veza, and R. Beuc, *J. Phys. B* **16**, 4619 (1983).

⁶G. Pichler, S. Milosevic, D. Veza, and D. D. Konowalow, *Chem. Phys. Lett.* **103**, 352 (1984).

⁷F. Engelke and H. Hage, *Chem. Phys. Lett.* **103**, 98 (1983).

⁸J. M. Brom, Jr. and H. P. Broida, *J. Chem. Phys.* **61**, 982 (1974); J. Tellinghuisen, G. Pichler, W. L. Snow, M. E. Hillard, and R. J. Exton, *Chem. Phys.* **50**, 313 (1980); Ya. P. Klyavinsh and M. L. Yanson, *Opt. Spectrosc. (USSR)* **52**, 376 (1982).

⁹L. Li and R. W. Field, *J. Phys. Chem.* **87**, 3020 (1983).

¹⁰G. Baumgartner, H. Kornmeier, and W. Preuss, *Chem. Phys. Lett.* **107**, 13 (1984).

¹¹T. Uzer and A. Dalgarno, *Chem. Phys.* **51**, 271 (1980).

¹²D. L. Cooper, J. M. Hutson, and T. Uzer, *Chem. Phys. Lett.* **86**, 472 (1982).

¹³X. Xie and R. W. Field, *Chem. Phys.* **99**, 337 (1985).

¹⁴X. Xie and R. W. Field, *J. Chem. Phys.* **83**, 6193 (1985).

¹⁵X. Xie and R. W. Field, *J. Mol. Spectrosc.* **117**, 228 (1986).

¹⁶Zh. L. Shvezhdza, S. M. Papernov, and M. L. Janson, *Chem. Phys. Lett.* **101**, 187 (1983).

- ¹⁷S. Milosevic and G. Pichler, *Z. Phys. D* **1**, 223 (1986); S. Milosevic, G. Pichler, E. Hasselbrinck, and R. Dueren, *Chem. Phys. Lett.* **128**, 145 (1986).
- ¹⁸J. T. Bahns and W. C. Stwalley, *Appl. Phys. Lett.* **44**, 826 (1984).
- ¹⁹D. D. Konowalow and J. L. Fish, *Chem. Phys.* **84**, 463 (1984).
- ²⁰I. Schmidt-Mink, W. Müller, and W. Meyer, *Chem. Phys.* **92**, 263 (1985).
- ²¹G. Ennen, Ch. Ottinger, K. K. Verma, and W. C. Stwalley, *J. Mol. Spectrosc.* **89**, 413 (1981).
- ²²L. Li, S. F. Rice, and R. W. Field, *J. Chem. Phys.* **82**, 1178 (1985).
- ²³P. Kusch and M. M. Hessel, *J. Chem. Phys.* **67**, 586 (1977).
- ²⁴W. Preuss and G. Baumgartner, *Z. Phys.* **320**, 125 (1985).
- ²⁵J. Tellinghuisen, *J. Mol. Spectrosc.* **103**, 455 (1984).
- ²⁶D. D. Konowalow, R. M. Regan, and M. E. Rosenkrantz, *J. Chem. Phys.* **81**, 4534 (1984).
- ²⁷J. Deoruard and N. Sadeghi, *Chem. Phys. Lett.* **111**, 353 (1984).
- ²⁸J. T. Bahns, Ph.D. thesis, University of Iowa, 1983.
- ²⁹D. Veza, S. Milosevic, and G. Pichler, *Opt. Commun.* **56**, 172 (1985).
- ³⁰D. Veza and C. Sansonetti (unpublished).