agree well with those given by M. Crance, J. Phys. B 11, 1931 (1978), and by Y. Gontier and M. Trahin, Phys. Rev. A 19, 264 (1979), and with the measured value of s.

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Observation of Bound-Free-Bound Triplet Absorption Bands in Li_2

Mark E. Koch and William C. Stwalley
Departments of Chemistry and Physics, The University of Iowa, Iowa City, Iowa 52242

and

Carl B. Collins
Department of Physics, University of Texas at Dallas, Richardson, Texas 75080
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Multiphoton ionization spectroscopy has yielded the first evidence for triplet absorption bands in Li_2 in the spectral region from 6215 to 5875 Å. This spectrum is the first of a new class of spectra resulting from a two-photon transition from a bound ($^3\Sigma_u^+$) van der Waals state to a previously unknown bound $^3\Lambda_u$ state (where $\Lambda = 0$, 1, or 2) through an intermediate free state ($^3\Pi_g$). The final state either autoionizes or collisionally forms the $^2\Sigma_g^+$ ground state of Li^{2+}.

The alkali-metal dimer triplet systems are of interest as potential excimer laser transitions since the lowest-lying triplet state, $^3\Sigma_u^+$, is very weakly bound.[1] Another point of possible practical as well as theoretical interest is that the lowest triplet state represents the interaction of spin-aligned lithium atoms, analagous to spin-aligned hydrogen atoms, a potential high-energy-density energy-storage medium.[2] Despite this interest, transitions between triplet states have either not been observed or not been analyzed because of experimental difficulties.[3] Lithium represents a special case since accurate *ab initio* calculations of its lowest-lying potential curves are available to aid in the analysis of new spectral features.[4-7] Correspondingly, these new calculations can be tested with new experimental results.

The techniques of absorption and fluorescence spectroscopy have yielded much information about the ground state, $^1\Sigma_g^+$, of the alkali metal dimers. However, the $^3\Sigma_u^+$ state has for the most part been inaccessible for spectroscopic investigation since the populations of the levels in this state are much smaller than those in the lower levels of the ground state. Moreover, even these lower levels, in transitions to higher electronic states, yield a confusion of overlapping bands.[8]

Two-photon spectra in alkali atoms and molecules have been detected via the method of ionization spectroscopy.[9,10] Since these spectra are detected only if excited-state product species are ionized, this method discriminates against the detection of absorptions to lower-lying energy levels. This detection method in its most sensitive variation, the space-charge ion detector, has been recently used in the investigation of photoionization of lithium vapor.[11] In a previous paper two of the present authors described both the method, "heat-pipe diode," and some preliminary results which established this new method's utility for the measurement of multiphoton ionization spectra.[12] Spectra from the red region, which will be discussed below, were not included in the earlier report.

An ionization spectrum from 5700 to 6300 Å is shown in Fig. 1(c). This was obtained with a heat-pipe diode at a lithium vapor pressure of 0.5 Torr with excitation by a chopped tunable dye laser (CR-599 operated broad band with <0.5 Å linewidth). The unsaturated signal of the molecular features depended upon the square of the light intensity indicating that two photons were absorbed to produce each ion. The atomic $2p$-to-$3d$ signal was more nearly a cubic than quadratic function of light intensity and was most probably due to the same ionization mechanism as the $2s$-to-$3d$ two-photon signal discussed previously.[11,12] For reference the neon optogalvanic

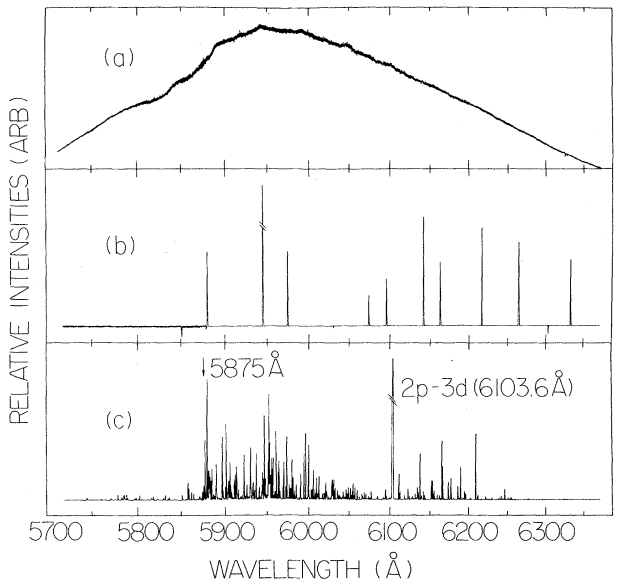

FIG. 1. (a) The intensity of the dye laser as monitored by the reference-channel photodiode in the CR-599 dye laser, (b) the optogalvanic neon reference spectrum, and (c) the new Li_2 system from the heat-pipe diode as functions of dye-laser wavelength.

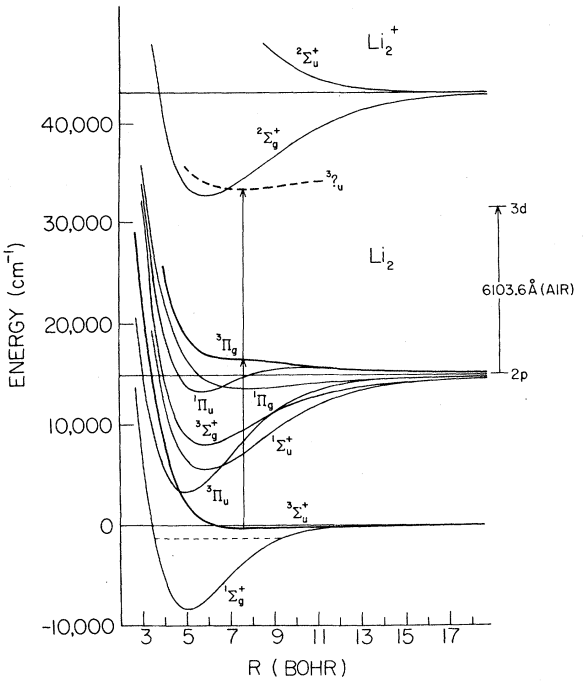

FIG. 2. The potential energy curves of Li_2 and Li_2^+ from Refs. 4–7 indicating (arrows) assignment of states involved in the new system.

spectrum from an Oriel spectral lamp (b) and the light intensity monitored from the CR-599 reference channel photoiode (a) were simultaneously recorded with this ionization spectrum on a three-pen chart recorder. Lockin amplifiers were used instead of the tuned amplifier mentioned in the earlier paper. This ionization spectrum was found to be markedly different from a simultaneous fluorescence spectrum which yielded an order of magnitude more lithium dimer features. The $2p$-to-$3d$ atomic transition yielded the only identifiable spectral feature which appeared in both types of spectra.[13]

The potential curves for Li_2 as shown in Fig. 2 contain unusual features which allow for the enhancement of triplet two-photon ionization over singlet two-photon ionization. In order to achieve two-photon transitions to states lying above the minimum of the ground state of Li_2^+ at wavelengths longer than 5875 Å it is necessary for the initial state to be a vibrational-rotational level lying near the common dissociation of the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states, i.e., above the dashed line in Fig. 2. Since the populations of these levels are comparable, the triplet two-photon transition will predominate over the singlet two-photon transition because of the resonant enhancement by the $^3\Pi_g$ dissociative intermediate state. There is no comparable enhancement in the singlet manifold. Furthermore, the near parallelism of the $^3\Pi_g$ and $^3\Sigma_u^+$ curves yields a classical band-system profile with a "head of heads" and sharp blue-end onset at 5875 Å. The final state of the transition is tentatively assigned as an *ungerade* triplet Rydberg state with an excited ion core (the $^2\Pi_u$ state of Li_2^+). This assignment leads to a high parallelism between all three states since the Rydberg potential $^3?_u$ (i.e., $^3\Lambda_u$ with $\Lambda = 0, 1$, or 2) should parallel the $^2\Pi_u$ Li_2^+ potential. It is, of course, possible that some part of the spectrum is due to transitions to the Li_2^+ ground state directly or to singlet-state transitions.

This two-photon transition from $^3\Sigma_u^+$ to $^3\Pi_g$ to $^3?_u$ in Li_2 apparently is the first observation of a bound-free-bound system. It is thus more amenable to analysis than a bound-bound-bound spectrum since in that case the condition of exact resonance allows for only a few transitions from initial to final levels to be observed. In this case, exact resonance is always possible because of the continuous range of intermediate-state energies. This new type of system should resemble a single-photon bound-bound spectrum with a resonant modulation of intensities due to the transition moment integrals between the upper and

lower states.

Several fortuitous occurrences discussed above allowed the observation of a two-photon triplet bound-free-bound band system in lithium with a single laser source. The present method, ionization spectroscopy, could easily be generalized for the study of other systems by the use of two independently tunable dye lasers. Various investigations of the multiplet and hyperfine structures, polarization dependence, and linewidths under high resolution (<3 MHz) using counterpropagating beams are under way at the Iowa Laser Facility. It is hoped that these will lead to the full identification of the final state, a rotational analysis including spin and hyperfine splittings, identification of the ionization mechanism, and finally a determination of the extent to which singlet-state transitions contribute to the signal.

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