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Space-charge ion detection of multiphoton absorption phenomena in lithium vapor

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The method of space-charge ion detection has been extended to the case of lithium. This was accomplished by the insertion of a space-charge-limited diode into a heat-pipe oven. Lithium vapor was probed with a N_2 laser-pumped tunable dye laser from 7150 to 4400 Å and with a Xe arc lamp from 7500 to 2300 Å. One- through four-photon events leading to ionization were observed. The atomic transitions observed were the principal series to $n = 10$ and the $2s$ to $3d$, $4s$, and $4d$ two-photon transitions. The two-photon absorption signals depended upon the third and fourth powers of the light intensity, indicating a new ionization process not heretofore considered important in diode signals. This new process appears to be excitation transfer from excited-state atoms to other excited-state atoms or molecules. For the high excited-state densities achieved in this experiment, this process appears to predominate over photoionization of excited-state atoms and other collisional processes involving excited-state and ground-state species. The $B \leftarrow X$, $C \leftarrow X$, and $D \leftarrow X$ molecular transitions, investigated by previous workers, were observed here.

I. INTRODUCTION

Laser-induced multiphoton absorption phenomena have been the subject of much recent theoretical and experimental interest.[1,2] The most appropriate methods identified for the acquisition of multiphoton absorption signals are fluorescence and ionization detection. In principal, since the latter is done *in situ*, it is more sensitive. When both can be implemented, fluorescence detection is complementary to ionization detection since it is sensitive to the particular excited state produced, whereas the latter method records an ionization event regardless of the excitation channel.

It is well known that the irradiation of an atomic or molecular vapor by light with less energy per quantum than the ionization energy of the relevant species can still produce ionization even when absorption is limited to single quanta.[3] This ionization is accomplished by various collisional processes involving atoms and molecules in excited states produced by absorptions of single photons. If the excited states are high enough in energy with respect to the ground state, the collisional processes become nearly 100% efficient. In addition to collisional ionization, direct photoionization of optically excited states must be considered. When the ion production rate is monitored as the wavelength of the illumination is continuously changed, a sequence of signals, an ionization spectra, corresponding to the probability of the absorption of photons by the atoms is obtained.

One device for detecting ions *in situ* is the space-charge ion detector, which, when combined with light modulation and synchronous detection, is capable of detecting ion production rates as low as a few ions per second.[4] This detector is a thermionic diode, which is filled with the vapor to be investigated. The diode is operated in the space-charge-limited mode in order to achieve electron current amplification of the photo-ion current. Since the presence of electrons in the interelectrode region of the diode establishes a potential barrier to further current flow, only a small leakage of electrons with energy above kT (filament) is allowed. A positive ion produced in this region is in a potential well and thus tends to stay in the well, while the associated electron will tend to diffuse to an electrode. The presence of the ion lowers the barrier potential, and many electrons subsequently flow across the diode. This valve is closed upon recombination of the ion with a space-charge electron or diffusion of the ion from the region of the potential well. The amplification factor thus obtained is approximately 10^5-10^6 electrons per ion.[5]

The space-charge detection method has recently been used in the investigation of various multiphoton processes in all the alkali metals except lithium.[6] The alkali metals are some of the simplest vapor systems for use in these detectors because of their unusually low work functions (~2.2 eV). The filament of the diode is most often tungsten with a work function of 4.4 eV. The electron emission from a hot filament depends exponentially upon the negative of its work function as described by the Richardson-Dushman equation, and consequently relatively high electron emissivities can be obtained for filaments partially covered with molten alkali. Even though the work function of the filament is lowered by partial coverage of the alkali metal, it is still above the work function of the plate, which is totally covered by alkali. This gives rise to a potential difference between the filament and the plate which increases the space-charge density, hence the amplification, and reduces the shot noise via space-charge smoothing. In the following material an extension of the space-charge detection method to the case of lithium is discussed, together with various results arising from the irradiation of the vapor with light from an N_2 laser-pumped tunable dye laser and a Xe arc lamp filtered by a 0.25-m Jarrel-Ash monochromator.

II. EXPERIMENTAL

In these experiments a heat-pipe oven was used in order to contain the lithium vapor. This provided all of the usual advantages of heat-pipe ovens plus great experimental flexibility in modifying the initial diode design. A schematic diagram of the heat-pipe diode, probe laser, and attendant electronics is shown in Fig. 1. The details of the construction and operation of heat-pipe ovens have been well described in the literature and will be reviewed only briefly here.[7] The pipe used in this work was a stainless-steel tube 60 long, with a 4.5-diameter, and with a 22-cm-long vapor zone. The stainless-steel mesh lining the pipe was lifted in the vicinity of the filament to give a smaller filament to plate distance near the optic axis. The filament, a 0.025-cm-diameter tungsten wire, was welded to 0.18-cm-diameter Kovar leads, which were in turn fused to a Corning 7052 tube for support. In operation the heat pipe, filled with Ar buffer gas, provides a lithium vapor of uniform pressure and temperature. Since the lithium flowing from the hot zone pushes against a plug of Ar gas at the cooled ends, the pressure of Li is identical to the Ar pressure while the temperature of Li is the temperature at which

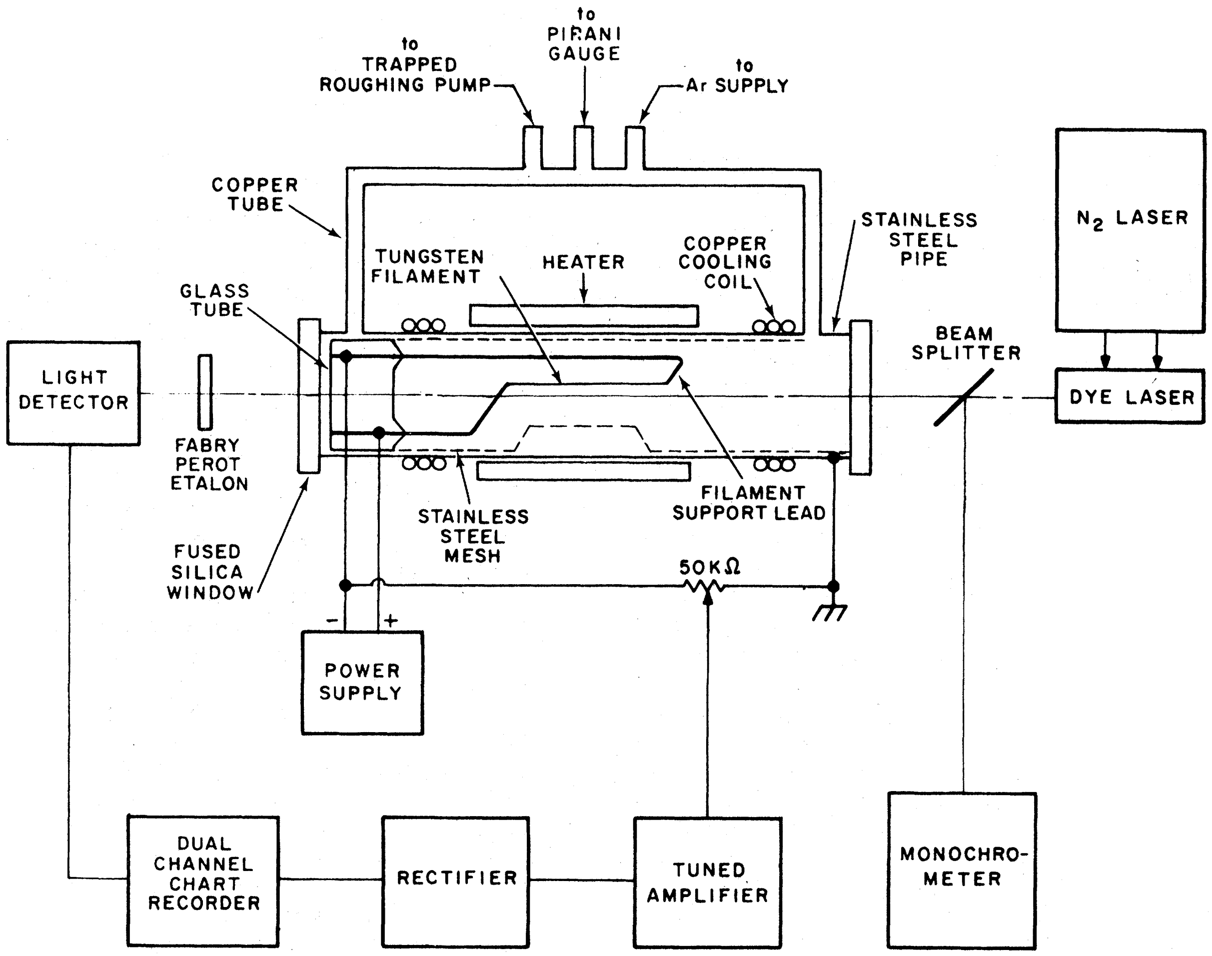

FIG. 1. Schematic of heat-pipe diode system with N_2 laser-pumped tunable dye laser source.

lithium has this vapor pressure. The diode was operated most often at a pressure of approximately 500 mtorr, though the range from 50 mtorr to 10 torr was surveyed briefly.

The electrical connections of the diode shown in Fig. 1 were as used in this experiment. The polarity of the filament power supply with respect to the diode signal connection is opposite to that found necessary in other alkali diodes. The result is that the filament will be held at a slightly less negative potential with respect to the plate owing to the voltage drop along the filament. However, this was not found to be a significant factor in improving either the signal level or the signal-to-noise ratio in the diode built in the manner described above.

The dye laser shown in Fig. 1 was of the Hansch type, consisting of a collinear arrangement of a broadband output coupler transmitting about 50% of the incident intensity, a quartz dye cell, a 22× beam expanding telescope, and an 1800 - lines/mm grating used in first order.[8] The dye cell was transversely pumped by a nitrogen laser constructed in this laboratory. It was a modified Blumlein type switched by a grounded-grid thyratron. In operation it produced about 700 kW peak power in 5-nsec pulses.[9] The output of the dye laser was a pulse of approximately 0.18 Å linewidth and 3–5 nsec duration. It was operated in the range 7150–4400 Å. A 1000-Xe arc lamp filtered by a 0.25-m Jarrel-Ash monochromator was also used. This source was chopped at the resonant frequency (8 Hz) of the tuned amplifier which was used to amplify the signal from the lithium diode. The amplifier had a Q of 80 and a gain of 10.[6]

The frequency of the dye laser was scanned by tilting the grating mounted in the Littrow position with a sine bar drive coupled to a stepping motor and driver. The motor was also used to scan the filter for the Xe arc lamp. After rectification the output from the amplifier was monitored on a strip-chart recorder giving the various spectra reported here. The signal of a transition as a function of light intensity was determined by tuning the appropriate spectral source to the transition and then inserting neutral-density filters in increments of 0.10 (density $= -\log_{10}$ transmission) and recording the corresponding signal.

III. RESULTS

In a scan from 8000 to 2400 Å, two spectral features were obtained with the Xe arc source. As shown in Fig. 2, the first of these was the principal series from $2s \rightarrow np$ for values of n from 4 to 10. These signals were the strongest obtained from the heat-pipe diode when obtained under low resolution. The $2s$ to $3p$ transition was absent even though the light intensity at that wavelength was larger than at the wavelengths of the other lines detected. Also produced with the arc source was a very weak signal shown in Fig. 3 corresponding to the X to C and X to D transitions in the lithium dimer. In the case of this signal the 0.25-m monochromator was used with 2000-μm slits to

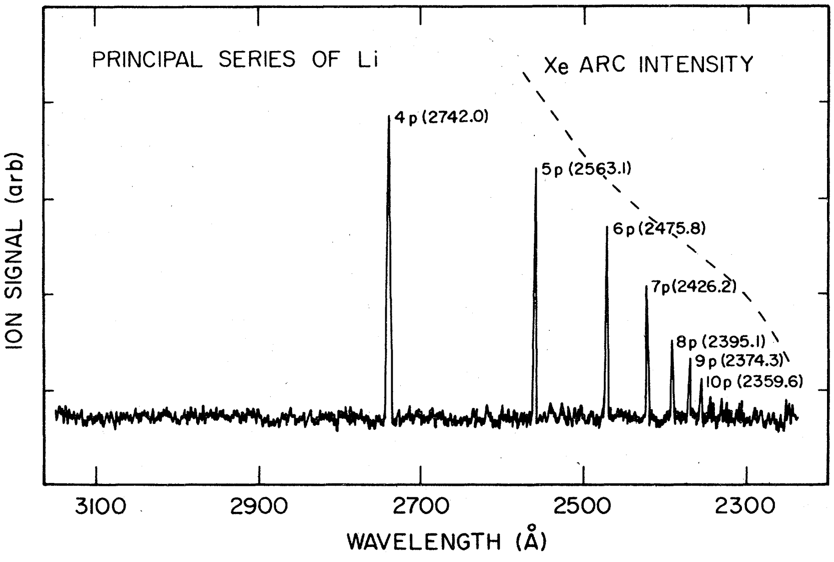

FIG. 2. Principal series in Li; excitation by a 1000-W Xe arc lamp filtered by a Jarrel-Ash 0.25-m monochromator with 150-μm slits (note the absence of the $2s$ to $3p$ line).

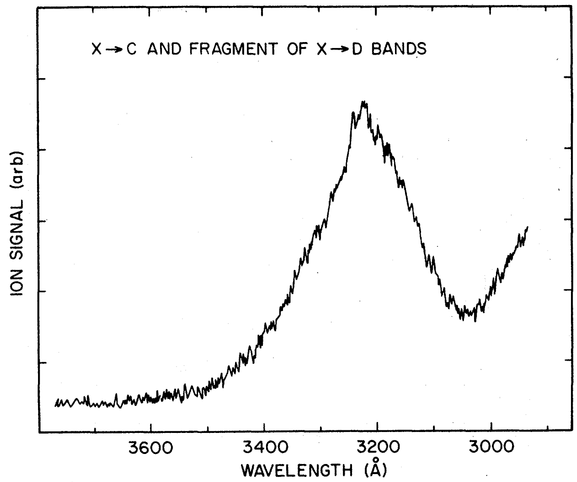

FIG. 3. *X* to *C* and *D* bands in Li_2; Xe arc lamp source filtered by a 0.25-M monochromator with 2000-μm slits.

produce a signal-to-noise ratio sufficient for a recording.

With the pulsed laser only three spectral features were obtained that could be attributed to two-photon transitions in atomic lithium. These are shown in Fig. 4. The strength of these fell by a factor of 1000 from the 2*s* to 3*d* to the 2*s* to 4*d* transitions. The identity of the 2*s* to 3*d* transition was verified by measurement of its wavelength to better than $\Delta\lambda = 0.15$ Å with a 3.4-m Jarrel-Ash spectrometer and that of the 2*s* to 4*s* transition by its extinction upon excitation by circularly polarized light of comparable intensity. The molecular features about the 2*s* to 4*s* line became more pronounced with pressure, indicating a possible collisional origin. The 2*s* to 4*d* transition occurs in a spectral region in which there is no molecular background ion signal. This region has been reported previously to exhibit no molecular absorption.[10] The appearance of the 2*p* to 4*d* line at 4607.9 Å was an artifact of the first diode built for this experiment. Although it appeared on many scans, it did not appear on scans from the diode described here. Since the filament-to-plate distance was smaller in the earlier diode, the *p*-state excitation was probably due to electron impact, as the electrons may pick up appreciable energy falling through the filament-to-plate potential difference. Therefore in small gap the energetic electrons are close to the optimal gain region in the space-charge region.

The detection of two-photon signals to principal quantum numbers higher than 4 was precluded by the exceptionally strong signal from the blue-green bands of Li_2. This system overlaps the two-photon ionization limit at the vacuum wavelength of 4599 Å. Figure 5 shows a scan of this system upon which is superimposed the positions of the band heads identified by earlier workers.[11] The *X* to *A* band system did not yield an ion signal strong enough for the resolution of component spectral features even though the laser was operated as far into the red as 7150 Å. Owing to the lack of an appreciable *X* to *A* signal, a new system or systems, presumably obscured in single-photon absorption spectra by the very strong *X* to *A* system, was observed. This system will be

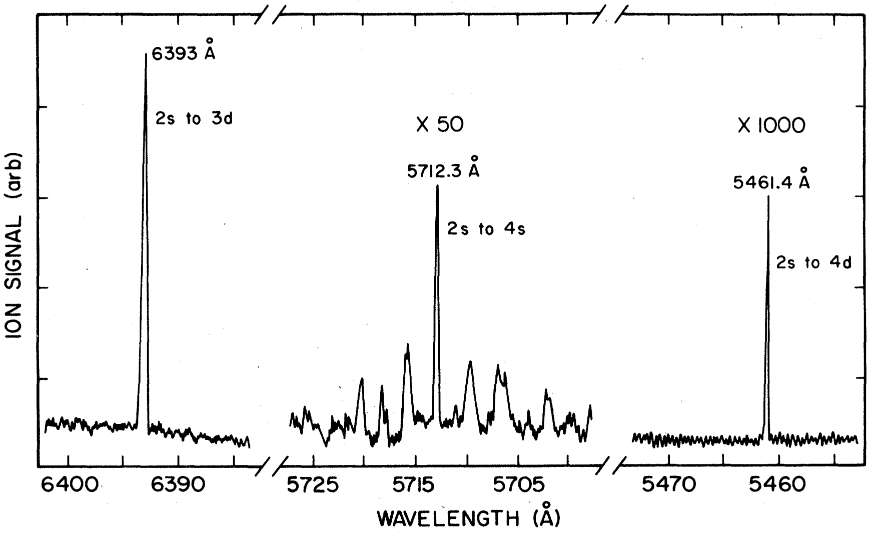

FIG. 4. Two-photon atomic lines in Li excited by N_2 laser-pumped tunable dye laser.

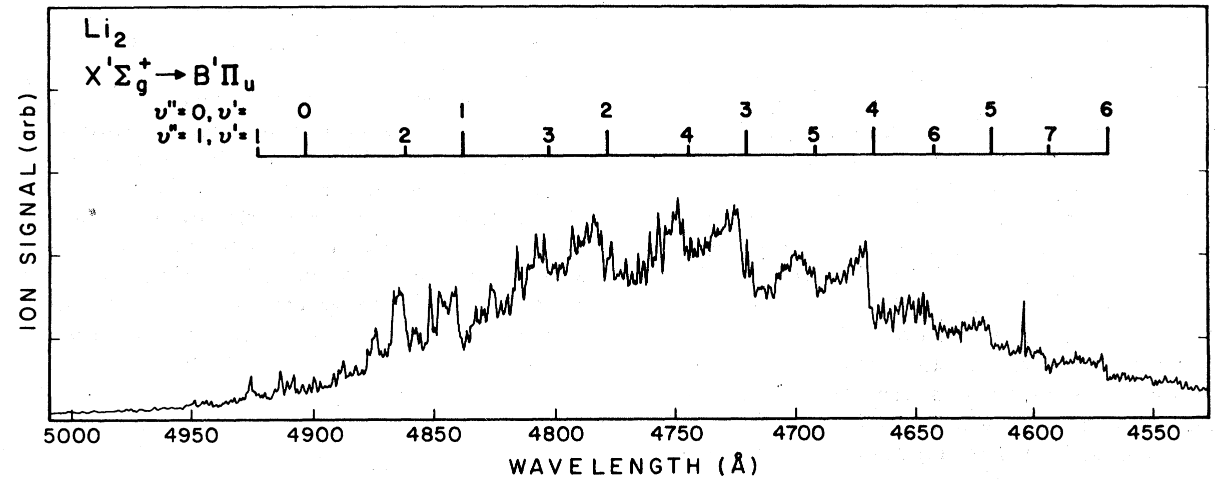

FIG. 5. Blue-green bands of Li_2; excitation with pulsed laser.

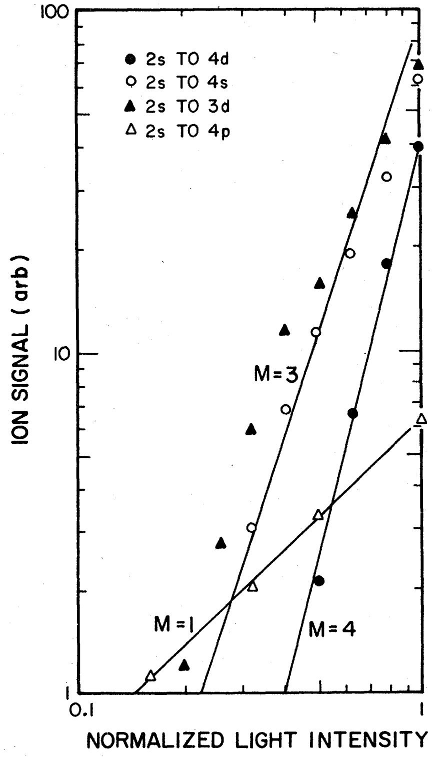

FIG. 6. Ion signal vs light intensity for atomic transitions.

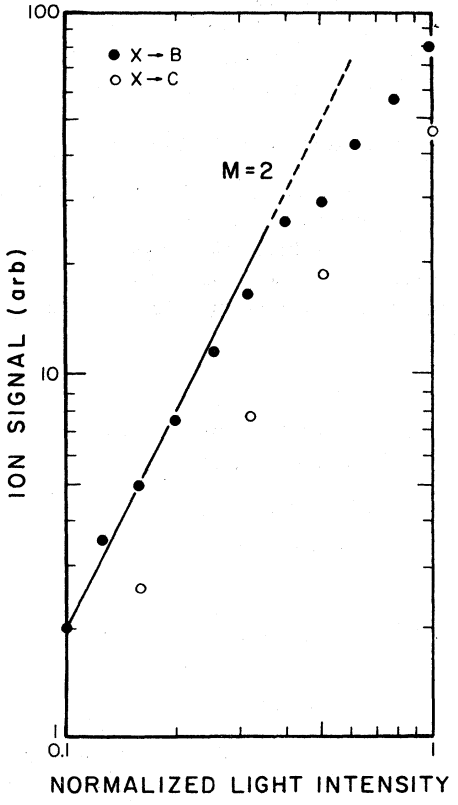

FIG. 7. Ion signal vs light intensity for molecular transitions.

the subject of a subsequent paper and will not be discussed further here.

Each of the signals mentioned earlier was recorded as a function of light intensity. The results are displayed on logarithmic axes in Figs. 6 and 7. The slope of the line which best fits the data for a particular transition gives an indication of the order of the process, i.e., the number of photons involved in producing each ion through the predominant ionization channel. The lines in these figures are for comparison with the data and do not represent statistical fits to the data. A least-squares fit to the $2s$ to $4d$ data, assuming a power-law dependence of the ion signal upon light intensity, gives a slope of 3.8 ±0.2 photons per ion. The other two-photon absorption signals were closer to three photons per ion, with some saturation of the ionization mechanism being evident. Conversely, the principal-series signals were unequivocably due to one photon per ion. These latter features provided a convenient calibration of the entire system, which was found to be linear over four decades of signal level. Of the molecular features, the X to C-band system ionization signal was found to depend upon the square of the light intensity. This two-photon ionization of the Li molecule with a non laser source gives a strong indication that the sensitivity of this diode was comparable to that of other alkali diodes.

IV. CONCLUSIONS AND SUMMARY

The processes leading to atomic ionization which have been identified as important in the heavier alkali metals are threefold. In the case of energy levels within kT of the ionization continuum, ordinary collisional ionization is the dominant mechanism:

$$A^* + A \rightarrow A^+ + A + e^- .$$

For lower-lying levels ionization may proceed by first molecular association,

$$A + A^* + A \rightarrow A_2^* + A,$$

followed by ion-pair formation,

$$A_2^* + A \rightarrow A^+ + A^- + A,$$

or for the lowest-lying levels by associative ionization,

$$A_2^* + A \rightarrow A_2^+ + A + e^- .$$

This last process explains the absence of the $2s$ to $3p$ transition in the principal-series spectrum as indicated in Fig. 2. From very accurate recent theoretical calculations of various Li_2^+ potentials, the $3p$ level can be shown to be below the minimum of the Li_2^+ ground potential and consequently cannot be associatively ionized.[12] This can be seen in Fig. 8, which gives potential curves and energy levels for Li_2 and Li.

The dependence of the $2s$ to $3s$ and $3d$ two-photon signals upon the cube of the light intensity could be ascribed to photoionization of the two-photon product state. However, the $2s$ to $4d$ signal clearly depends on the fourth power of light intensity. A reasonable explanation for this dependence is that ionization occurs by excitation transfer from one two-photon product state atom to another. The rate of ionization would therefore be

$$\frac{dn^+}{dt} = k(n^*)^2 ,$$

where n^+ is the ion concentration, k a reaction-

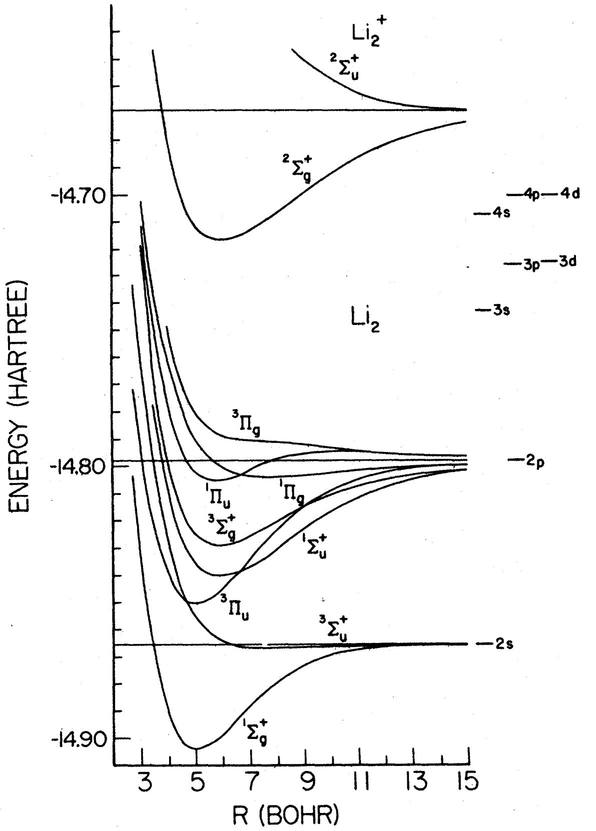

FIG. 8. Li_2 potential curves and superposed Li energy levels. Potential curves for Li_2 are from accurate *ab initio* calculations (Ref. 13–15), curves for Li_2^+ from model potential calculations (Ref. 12).

rate constant, and n^* the excited-state atom concentration. Since the concentration of two-photon product state atoms produced is dependent on the square of the light intensity, the rate of this reaction must depend upon the fourth power of light intensity. This dependence of the signal upon the light intensity indicates the predominance of this process over either photoionization of the two-photon product state atoms or associative ionization. Therefore it is likely that a similar process is responsible for the 2*s* to 3*d* and 2*s* to 4*s* ion signals. Since the 2*s* to 4*d* transition is in a spectral region with little or no molecular excitation and the other two lines occur outside this region, the dependence of these signals on a different power of light intensity might be due to excitation transfer between atoms in two-photon product states and excited-state molecules. This process would have a rate given by

$$\frac{dn^+}{dt} = k' n^*_{\mathrm{atm}} n^*_{\mathrm{mol}}$$

and would thus depend upon the cube of the light intensity, since the molecular excited-state concentration is due to a single-phototon absorption. A study of the pressure dependence of the two-photon ion signal was not possible here, since the dependence of the detector sensitivity upon pressure is a complex function of several pressure-temperature parameters. Moreover, since the heat-pipe operation depends upon the lithium existing as a saturated vapor, the pressure and temperature are not independent variables. Such a study would have interesting consequences, however, since the pure atomic versus the atomic-molecular ionizing collision would depend upon pressure differently.

A calculation of the ionization rate for the 2*s* to 3*d* transition lends further support to the excitation transfer scheme. In this calculation, it is assumed that the collisional ionization process is negligible to radiative decay in the deexcitation of the atoms and molecules. Since the X to B system signal showed strong saturation, it is further assumed that the X to A transition was saturated. This gives a concentration of the order of 10^{11} excited-state-molecules/cc. Since the ion signal from the 2*s* to 3*d* transition is a large signal, a concentration of 10^{11} 3*d*-state atoms is also assumed. If a cross section of 10 Å^2 is assumed for the excitation transfer, then with the above assumptions and given a beam waist of 10^{-4} cm^2 the ion production rate is ~20 ions/sec. Although this is a detectable rate, it cannot account for the very large 2*s* to 3*d* ion signal. A further enhancement of the ion production rate could be attributed to a larger number of 3*d*-state atoms than estimated, but then this would lead to a predominance of the four-photon over the three-photon mechanism which would contradict the data. However, if the transfer cross section from a 3*d* atom to an A-state molecule were resonantly enhanced, the molecular process might dominate the atomic process. Thus, the coincidence of a higher atomic excited-state concentration with the resonant enhancement process would lead to a signal of the proper order of magnitude.

In conclusion, the heat-pipe diode has been shown to be a sensitive new device for use in the investigation of multiphoton absorption phenomena in lithium vapor.[16] Several spectral features previously observed with classical absorption techniques, but perhaps with more experimental difficulty than that encountered here, were observed with this system. In addition to these, a new feature was observed due in part to unique properties of Li and Li$_2$ which contributed relatively low levels of molecular ion signals at 5460 Å, and in part to the added power of ionization spectroscopy as contrasted with fluorescence spectroscopy. This feature, a four-photon ionization process involving two-photon atomic absorptions, indicates a new ionization channel via collisional transfer of excited-state energy from one excited-state atom or molecule to another.

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