unlikely that the $J=4 \rightarrow J=4$ component makes any contribution to the observed 4715-Å signal.

The experimentally observed line shape for the laser-induced charge-transfer process is narrower and more symmetric, and occurs closer to the energy defect of the infinitely separated atoms, than is expected on the basis of a Landau-Zener curve-crossing model.[1,2,4] The similarity of the polarizabilities[20] of ground-state Ca and ground-state Sr imply quite parallel potentials for the initial and final quasimolecular states, and a shallow crossing at large $R$. This situation probably requires a calculation along the lines of Copeland and Tang[3] or Rapp and Francis.[21]

Ground-state ions are easily created and represent a means of long-lived energy storage. Laser-induced charge-transfer collisions provide a technique for selectively and rapidly channeling this energy into a designated excited state.

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# Pulsed Optical-Optical Double Resonance Spectroscopy of *Gerade* Excited Electronic States in $Li_2$

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Optical-optical double resonance using two nitrogen-laser–pumped dye lasers has been used to make the first spectroscopic study of the hitherto unobserved *gerade* excited electronic states of $^7Li_2$. Three $^1\Sigma_g{}^+$ and two $^1\Pi_g$ states are observed. Molecular constants in $cm^{-1}$ for one of the $^1\Pi_g$ states are $T_e = 31\,868.02$, $\omega_e = 229.71$, $\omega_e X_e = 1.654$, $B_e = 0.469\,86$, $\alpha_e = 0.005\,959$, $D_e = 7.301$, and $r_3 = 3.198$ Å.

Interest in the electronic structure of $Li_2$ dates from the time of the earliest application of quantum mechanics to molecular structure.[1] After molecular hydrogen, $Li_2$ is the least complex of the stable homonuclear diatomic molecules, and its electronic structure continues to be of funda-

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mental importance as well as finding practical use as a laser medium. The $X\,^1\Sigma_g{}^+$ ground state has received extensive theoretical[2] treatment and experimental examination.[3] Of the excited electronic states, those which correlate with one $2s$ and one $2p$ lithium atomic state have received most attention theoretically[4] and experimentally with the $A\,^1\Sigma_u{}^+$ and $B\,^1\Pi_u$ states well characterized.[2,3] Some experimental information exists for the excited $C\,^1\Pi_u$ and $D\,^1\Pi_u$ states,[5] but none of the excited *gerade* states have been observed since their excitation from the ground state is forbidden for normal one-photon absorption.

For homonuclear diatomic molecules, pulsed optical-optical double-resonance spectroscopy offers an attractive approach to the discovery and study of new electronic states having the same inversion symmetry as the ground state. In $Li_2$ the stepwise two-photon excitation to *gerade* states from the $X\,^1\Sigma_g{}^+$ state is allowed. Furthermore, the pulsed mode of excitation allows one to control the extent of rotational relaxation in the intermediate states, resulting in spectra that can be quickly and unambiguously assigned. In this work we describe the first spectroscopic examination of the excited *gerade* states and present molecular constants for one of the new $^1\Pi_g$ states.

The experimental arrangement is shown schematically in Fig. 1. The cell is a heat-pipe oven[6] initially filled with several grams of lithium (99.99% $^7$Li) and 1.3 kPa (10 Torr) of helium and subsequently operated at 750°C. Electronic excitation is produced by two tunable dye lasers pumped by a 1-MW nitrogen laser. The pump dye laser was operated with an output of approximately 0.02 mJ/pulse, while the probe dye laser

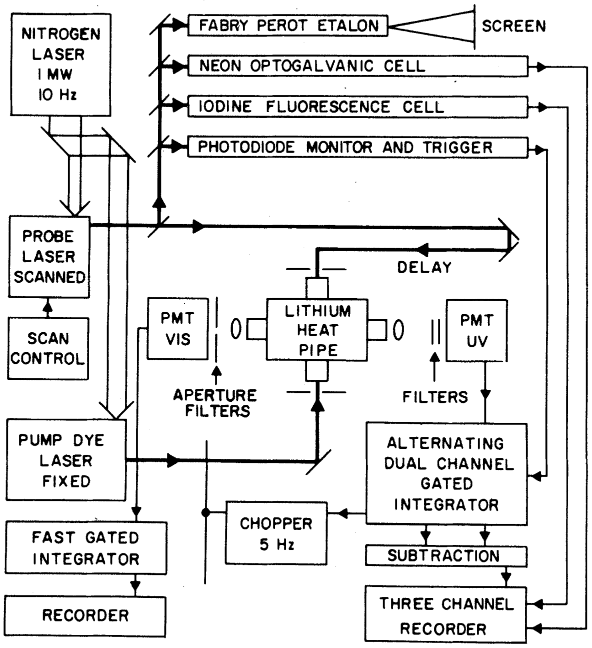

FIG. 1. Schematic diagram of the experimental arrangement for performing pulsed optical-optical double-resonance spectroscopy on $^7Li_2$ using ultraviolet fluorescence detection and signal treatment in which spectral features originating from only one of the two dye lasers are subtracted before final recording.

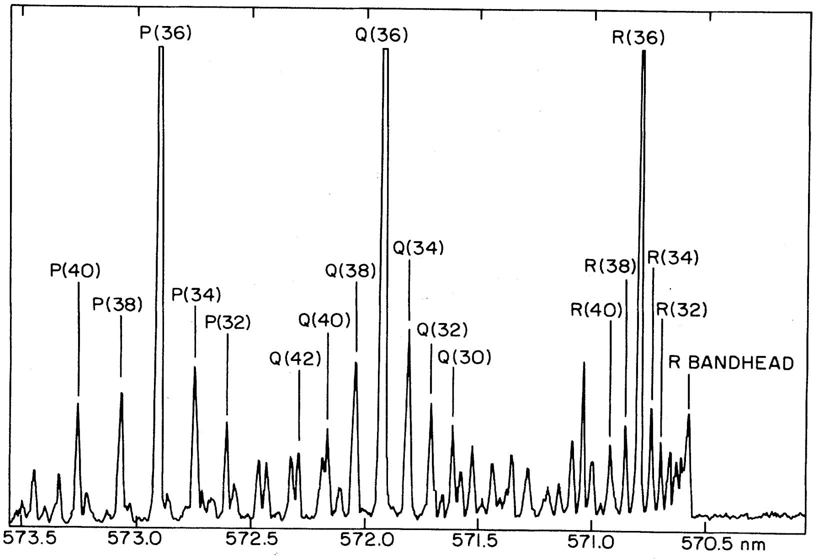

FIG. 2. Optical-optical double-resonance excitation of the $^1\Pi_g$ ($v=1$) band following pumping of the $A\,^1\Sigma_u{}^+$ ($v=2$, $J=36$) level of $^7Li_2$. The wavelength scale is the probe-laser wavelength.

was operated with up to 0.13 mJ/pulse depending upon the wavelength. The linewidth of both lasers was 0.2 cm$^{-1}$. The pump dye laser is tuned to excite a selected level of the $A\,^1\Sigma_u^+$ state, and the wavelength of the probe dye laser is scanned to produce further excitation from the intermediate $A\,^1\Sigma_u^+$ state to higher-energy *gerade* states. The probe laser pulse is optically delayed, controlling the amount of rotational relaxation in the $A\,^1\Sigma_u^+$ state before excitation to the final *gerade* states. Ultraviolet emission is produced when the final *gerade* state energy is comparable to or above the $C\,^1\Pi_u$ state at 30 500 cm$^{-1}$ and apparently originates from collisional transfer from the *gerade* state to the $C\,^1\Pi_u$ state with subsequent fluorescence to the ground state. Ultraviolet detection is used to record the laser excitation spectrum of these states while visible detection is necessary to observe those *gerade* states that are less energetic than the $C\,^1\Pi_u$ state.[7]

Both dye lasers are excited by the nitrogen laser which is pulsed at 10 Hz. However, the pump laser beam is also chopped at 5 Hz permitting subtraction from the excitation spectrum of all signals not dependent upon *both* dye lasers. Although pulsed optical-optical double resonance has been utilized previously,[8] the additional feature of subtracting all two-photon excitations originating from the scanned laser alone produces a very useful additional simplification of the spectrum. Following the subtraction of the unwanted spectral features, the ${}^7\mathrm{Li}_2$ optical-optical double-resonance excitation spectrum is recorded together with the optogalvanic[9] spectra of neon and argon for wavelength calibration. Some regions of the ${}^7\mathrm{Li}_2$ spectrum were also recorded with the visible fluorescence spectrum of $I_2$.

A typical vibrational band of the excitation to a ${}^1\Pi_g$ state is shown in Fig. 2 where the optical delay is adjusted to permit some rotational relaxation in the intermediate $A\,^1\Sigma_u^+$ state. The strong $P$, $Q$, and $R$ lines originating from the $A\,^1\Sigma_u^+$ rotational level being pumped are easily distinguishable from the other components. In collecting data for the observed *gerade* states, the following levels of the $A$ state were used: $v=7$, $J=22$; $v=7$, $J=8$; $v=7$, $J=13$; $v=2$, $J=36$; $v=1$, $J=20$; and $v=0$, $J=18$. A total of 181 transitions from these intermediate states to vibrational levels from $v=0$ to $v=11$ of the lowest ${}^1\Pi_g$ state observed in this work were recorded. A least-squares procedure and the published $A\,^1\Sigma_u^+$ state results[3] were used to obtain the molecular constants shown in Table I. Spectral line positions calculated from these constants reproduce the observed spectrum with a standard deviation of 1.4 cm$^{-1}$.

TABLE I. Molecular constants of a ${}^1\Pi_g$ state of ${}^7\mathrm{Li}_2$ determined by pulsed optical-optical double-resonance spectroscopy. Error limits are standard deviations.

| Constant | |
|---|---|
| $T_e$ | 31 868.02±0.49 cm$^{-1}$ |
| $\omega_e$ | 229.71±0.15 cm$^{-1}$ |
| $\omega_e x_e$ | 1.654±0.011 cm$^{-1}$ |
| $B_e$ | 0.469 86±0.000 80 cm$^{-1}$ |
| $\alpha_e$ | 0.005 96±0.000 10 cm$^{-1}$ |
| $D_e$ | (7.30±0.33)×10$^{-6}$ cm$^{-1}$ |
| $r_e$ | 3.198±0.003 Å |

In the present study the energy range from 27 000 to 40 000 cm$^{-1}$ above the ground state of $\mathrm{Li}_2$ was investigated using various levels of the $A\,^1\Sigma_u^+$ state as intermediate levels. In this region one additional ${}^1\Pi_g$ state and three ${}^1\Sigma_g$ states were also observed; these will be discussed in future publications.

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