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Dissociation Energy of Li_2 from Laser-Excited Fluorescence*

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The fluorescence spectra $B\ ^1\Pi_u-X\ ^1\Sigma_g^+$ of the molecular species $^6\text{Li}_2$, $^6\text{Li}^7\text{Li}$, and $^7\text{Li}_2$, excited by the cw lines of the argon ion laser, have been observed and analyzed. Based on a short Birge-Sponer extrapolation of the vibrational levels of the ground state, the dissociation energy for the Li_2 molecule has been determined to be $D_0^0 = 1.026 \pm 0.006$ eV. This value, combined with the dissociation limit of the upper state determined by Loomis and Nusbaum, proves that there is a hump of about 0.12 ± 0.04 eV above the asymptote of the potential curve of the $\text{Li}_2\ B\ ^1\Pi_u$ state. Improved rotational and vibrational constants of the ground state of Li_2 have also been obtained. A new technique is described which utilizes collision-induced rotational transfer to facilitate the v' , J' assignment of the excited levels.

INTRODUCTION

The dissociation energy of the Li_2 molecule has been the subject of some controversy for many years. The first determination of its value was made by Wurm¹ as a result of his study of the fluorescence spectrum excited by sunlight, and involved a Birge-Sponer extrapolation from $v''=9$. The value obtained ($D_0^0 = 1.69$ eV) was in rather good agreement with quantum-mechanical calculations performed by Delbrück² at about the same time (1.4 eV).

In 1931, Loomis and Nusbaum³ observed and analyzed the magnetic rotation spectrum of Li_2 . From a short extrapolation of the vibrational structure of the $B\ ^1\Pi_u$ excited state they obtained a value of $D_0^0 = 1.14 \pm 0.03$ eV, which again was in agreement with new quantum-mechanical calculations (1.09 eV) published by Bartlett and Furry.⁴

Lewis,⁵ using a molecular-beam method,⁶ determined the dissociation energy of Li_2 to be $D_0^0 = 1.03 \pm 0.04$ eV. However, the limits of error of his results as well as

those of Loomis and Nusbaum were still broad enough that the spectroscopic and thermochemical measurements could be possibly reconciled.

The good agreement observed between theoretical and experimental values in the earliest investigations was later shown to be fortuitous. James⁷ has pointed out that the theoretical calculations omitted the effect of the antibonding $1s\sigma_u$ electrons. When this contribution is considered, the best Heitler-London calculations give a value of D_0^0 around 0.3 eV, and only with a variational treatment can this value be improved to 0.5 eV. Detailed configuration interaction calculations by Ishiguro *et al.*⁸ have increased the theoretical value of D_0^0 to 0.77 eV, and only recently Das and Wahl⁹ have been able to obtain a value of $D_0^0 = 0.91$ eV by combining the SCF method with superposition of configurations.

The best spectroscopic value³ of D_0^0 was deduced by subtracting the energy of the atomic $2p$ electron from the dissociation limit of the $B\ ^1\Pi_u$ state. This result depends on the accuracy of the dissociation limit determination and on the assumption that the $B\ ^1\Pi_u$ potential curve does not have a hump at large internuclear distances. However, King and Van Vleck¹⁰ have predicted such a potential hump in excited states of homonuclear diatomic molecules. For example, a hump was predicted for the $B\ ^1\Pi_u$ state of Na_2 , but has not been clearly confirmed experimentally.¹¹ If an analogous hump really exists in the $B\ ^1\Pi_u$ state of Li_2 , it could explain the discrepancy between spectroscopic and thermochemical values of D_0^0 .

Evans *et al.*¹² have suggested that Lewis' result is

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¹ K. Wurm, *Naturwiss.* **16**, 1028 (1928).

² M. Delbrück, *Ann. Physik* **5**, 36 (1930).

³ F. W. Loomis and R. E. Nusbaum, *Phys. Rev.* **38**, 1447 (1931).

⁴ J. H. Bartlett and W. H. Furry, *Phys. Rev.* **38**, 1615 (1931).

⁵ L. C. Lewis, *Z. Physik* **69**, 786 (1931).

⁶ In Lewis' method an alkali beam, effusing from a Knudsen cell at known temperature, passes through an inhomogeneous magnetic field. By deflecting the alkali atoms out of the beam, the ratio of the undeflected alkali dimer molecules to the alkali atoms was determined. This ratio, together with the total vapor pressure taken from the literature, gives the equilibrium constant K for the alkali dimerization at the oven temperature T . From the value of K at a temperature T the dissociation energy D_0^0 may be found using the partition function of the molecule. Alternatively, after performing the measurement of K at different temperatures the heat of dissociation is found from the slope of a plot of $\ln K$ vs $1/T$. The value of D_0^0 is then obtained by correcting for the variation of the heat of dissociation with temperature.

⁷ H. M. James, *J. Chem. Phys.* **2**, 794 (1934).

⁸ E. Ishiguro, K. Kayama, M. Kotani, and I. Mizuno, *J. Phys. Soc. Japan* **12**, 1355 (1957).

⁹ G. Das and A. C. Wahl, *J. Chem. Phys.* **44**, 87 (1966).

¹⁰ G. W. King and J. H. Van Vleck, *Phys. Rev.* **55**, 1165 (1939).

¹¹ The predicted hump would be about 0.1 eV and the difference between the spectroscopic [F. W. Loomis and R. E. Nusbaum, *Phys. Rev.* **40**, 384 (1932)] and the thermochemical (Ref. 5) values of D_0^0 is of the order of 0.02 eV and is within the experimental errors. P. Kusch and M. M. Hessel, *J. Mol. Spectry.* (to be published) present evidence for a slight potential barrier in the $B\ ^1\Pi_u$ state of Cs_2 .

¹² W. H. Evans, R. Jacobson, T. R. Munson, and D. D. Wagman, *J. Res. Natl. Bur. Std.* **55**, 83 (1955).

incorrect, perhaps due to the use of impure lithium samples, and they have deduced that the true thermochemical value for D_0^0 of Li_2 must be 1.113 ± 0.006 eV, in agreement with the spectroscopic value of Loomis and Nusbaum. If this value is correct, it would imply that the potential hump in the $B^1\Pi_u$ state is rather small or nonexistent. In recent reviews¹³ on the dissociation energies of diatomic molecules, sometimes the 1.03 value is accepted as the correct one, sometimes 1.14, and sometimes the average.

In view of this ambiguous situation it seems worthwhile to attempt a direct spectroscopic determination of D_0^0 from a study of the vibrational structure of the ground state of Li_2 .

EXPERIMENTAL

A promising possibility for this kind of investigation is the study of the fluorescence spectrum of Li_2 , in which transitions to high-lying vibrational levels of the ground state might be expected to occur. The cw argon-ion laser lines between 4500 and 5200 Å fall within the $B^1\Pi-X^1\Sigma_{u_g}^+$ blue-green band system of the Li_2 molecule. Recent fluorescence experiments utilizing laser lines as a source of excitation have already proved successful for the alkali dimer molecules Na_2 ,¹⁴ K_2 ,¹⁵ Rb_2 , and Cs_2 .¹⁶ Overlap between a laser line and a molecular absorption line is less likely in Li_2 than in the previously studied molecules because of the more open structure of the Li_2 spectrum. However, the use of the two isotopes ^6Li and ^7Li is a compensating factor. In this way, three different molecular species can be studied and the probability of overlap is correspondingly increased. We find that the prominent argon-ion laser lines excite, on the average, one strong transition in each of the three molecular species.

Lithium samples were obtained from the Oak Ridge National Laboratory. Their stated isotopic purities were 99.99% for ^7Li and 95.6% for ^6Li . Samples of one isotopic species or 1:1 mixtures of both (to produce $^6\text{Li}^7\text{Li}$ molecules) were placed in the fluorescence cell, a small tantalum-lined stainless-steel cylinder that was externally heated. The laser light entered and left this cylinder through steel tubes 20 cm in length and 0.9 cm

in diameter, with windows mounted at the ends. The fluorescence light was observed at right angles through a third tube, which was 24 cm in length and 2.8 cm in diameter. These three tubes had a small wall thickness of 0.03 cm. This design kept the lithium from depositing on the windows and prevented their overheating. The cylinder was heated with nichrome windings to a temperature between 650 and 750°C. At a temperature of 650°C, the total vapor pressure is 0.17 torr, and the Li_2 molecules constitute 2% of the vapor.¹⁷

The fluorescence was excited with the argon-ion laser lines at 4579.4, 4764.9, 4879.9, 4965.1, and 5145.3 Å.¹⁸ The spectra were first photoelectrically scanned with a Czerny-Turner SPEX spectrometer and then photographed on Eastman-Kodak 103a-F plates with the same instrument in the first order (reciprocal dispersion about 11 Å/mm). The photographic spectra gave the higher resolution and the photoelectric spectra the higher sensitivity. The region from 4000 to 7000 Å was studied photographically using the neon spectrum as a calibration standard of wavelengths. The line positions were measured with a photoelectric comparator.¹⁹ A computer program²⁰ was used to calculate the vacuum wavenumbers of the observed lines from those of the neon lines. The relative accuracy (for lines of medium intensity) was ± 0.2 cm⁻¹. Most of the lines were measured on two or three different plates and the mean values of their wavenumbers were used for the analysis of the spectrum.

RESULTS AND ANALYSIS

Owing to the $^1\Pi$ character of the upper state, two types of fluorescence series are observed¹⁴: Q series if the laser line excites a transition with $\Delta J=0$ (Q line) and P - R doublets if the excitation occurs on an R or P line, $\Delta J=\pm 1$. Table I is a summary of the series we have observed and analyzed. Other weaker series were also observed photoelectrically but were not studied in detail. The intensity of the lines within each series varies considerably and in an irregular pattern. For most of the series only some of the lines appear on the photographic plates; the weaker ones are observed only with very high gain in the recording spectrometer, and some are completely absent. In the course of the analysis only the photographically observed lines are used. Two examples of the fluorescence series observed are presented in Tables II and III.

In several cases the members of the fluorescence

¹³ For example, A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall Ltd., London) recommends $D_0^0=1.12 \pm 0.05$ eV in his first edition (1947), $D_0^0=1.03 \pm 0.03$ eV in his second edition (1953), and $D_0^0=1.12 \pm 0.03$ eV in his third edition (1968). On the other hand, P. G. Wilkinson, [*Astrophys. J.* **138**, 778 (1963)] prefers Lewis' thermochemical value, $D_0^0=1.03$, whereas E. U. Condon, in *Handbook of Physics*, E. U. Condon and H. Odishaw, Eds. (McGraw-Hill Book Co., New York, 1967), pp. 7-105, adopts the average value, $D_0^0=1.08$ eV.

¹⁴ W. Demtröder, M. McClintock, and R. N. Zare, *J. Chem. Phys.* **51**, 5495 (1969), this issue.

¹⁵ W. J. Tango, J. K. Link, and R. N. Zare, *J. Chem. Phys.* **49**, 4264 (1968).

¹⁶ M. McClintock and L. C. Balling, *Bull. Am. Phys. Soc.* **13**, 55 (1968).

¹⁷ T. B. Douglas, C. F. Epstein, J. L. Dever, and W. H. Howland, *J. Am. Chem. Soc.* **77**, 2144 (1955).

¹⁸ W. B. Bridges and A. N. Chester, *IEEE J. Quantum Electron.* **1**, 66 (1965).

¹⁹ We thank Dr. C. Keith McLane, National Bureau of Standards, Boulder, Colorado, for the use of the comparator microdensitometer.

²⁰ We wish to express our appreciation to Dr. Carl Love, National Bureau of Standards, Boulder, Colorado, for making his computer programs available to us.

TABLE I. The strong Li₂ fluorescence series excited by the argon-ion laser lines.

| Molecule | Exciting line (Å) | Excitation process | | | | Observed fluorescence progressions | |
|---------------------------------|-------------------|--------------------|------------|-----------|-----------|------------------------------------|---------------------|
| | | <i>v''</i> | <i>J''</i> | <i>v'</i> | <i>J'</i> | Lines | Range of <i>v''</i> |
| ⁷ Li ₂ | 4765 | 1 | 24 | 4 | 24 | Q(24) | 0-12* |
| ⁷ Li ₂ | 4880 | 1 | 30 | 2 | 31 | R(30), P(32) | 0-8 |
| ⁷ Li ₂ | 5145 | 5 | 29 | 3 | 30 | R(29), P(31) | 0-8 |
| ⁷ Li ₂ | 5145 | 9 | 37 | 9 | 38 | R(37), P(39) | 3-18 |
| ⁷ Li ₂ | 5145 | 7 | 61 | 7 | 61 | Q(61) | 0-18 |
| ⁶ Li ⁷ Li | 4765 | 2 | 8 | 5 | 9 | R(8), P(10) | 1-13 |
| ⁶ Li ⁷ Li | 4965 | 0 | 45 | 0 | 45 | Q(45) | 0-5 |
| ⁶ Li ₂ | 4765 | 3 | 31 | 9 | 31 | Q(31) | 2-19 |
| ⁶ Li ₂ | 4765 | 5 | 28 | 11 | 29 | R(28), P(30) | 2-21 |
| ⁶ Li ₂ | 4880 | 0 | 40 | 1 | 41 | R(40), P(42) | 0-7 |
| ⁶ Li ₂ | 5145 | 3 | 40 | 1 | 41 | R(40), P(42) | 0-7 |
| ⁶ Li ₂ | 5145 | 4 | 46 | 3 | 45 | R(44), P(46) | 0-8 |

* As a result of energy transfer produced by collisions, Q series with *J''*=20, 22, 26, and 28 and P-R series with *J'*=21, 23, 25, and 27, were also observed photographically and used in the general analysis of the spectrum.

TABLE II. The fluorescence series of ⁷Li₂ excited with λ=4880 Å (20 487 cm⁻¹).

| Vibrational transition (<i>v'-v''</i>) | Rotational line | <i>ν</i> _{obs} (cm ⁻¹) | Relative intensity | <i>ν</i> _{calc} ^a (cm ⁻¹) | <i>ν</i> _{obs} - <i>ν</i> _{calc} |
|--|-----------------|---|--------------------|---|--|
| 2-0 | R(30) | 20 826.7 | 8 | 20 826.8 | -0.1 |
| 2-0 | P(32) | 20 744.9 | 10 | 20 744.9 | 0.0 |
| 2-1 | R(30) | 20 487.0 | Laser | 20 487.0 | 0.0 |
| 2-1 | P(32) | 20 406.2 | 7 | 20 406.0 | 0.2 |
| 2-2 | R(30) | 20 152.7 | 8 | 20 152.5 | 0.2 |
| 2-2 | P(32) | 20 072.7 | 8 | 20 072.5 | 0.2 |
| 2-3 | R(30) | ... | | | |
| 2-3 | P(32) | ... | | | |
| 2-4 | R(30) | 19 500.2 | 7 | 19 500.0 | 0.2 |
| 2-4 | P(32) | 19 422.0 | 7 | 19 421.8 | 0.2 |
| 2-5 | R(30) | 19 182.3 | 15 | 19 182.0 | 0.3 |
| 2-5 | P(32) | 19 105.1 | 12 | 19 104.7 | 0.4 |
| 2-6 | R(30) | 18 869.4 | 10 | 18 869.4 | 0.0 |
| 2-6 | P(32) | 18 793.2 | 10 | 18 793.2 | 0.0 |
| 2-7 | R(30) | 18 562.4 | 7 | 18 562.5 | -0.1 |
| 2-7 | P(32) | 18 487.2 | 7 | 18 487.3 | -0.1 |
| 2-8 | R(30) | 18 261.1 | 4 | 18 261.3 | -0.2 |
| 2-8 | P(32) | 18 186.8 | 3 | 18 187.1 | -0.3 |

* With the molecular constants deduced in the course of this work (Table IV).

TABLE III. Fluorescence series of ⁶Li₂ excited with λ=4880 Å and λ=5145 Å (20 487 and 19 430 cm⁻¹).

| Vibrational transition (<i>v'-v''</i>) | Rotational line | <i>ν</i> _{obs} (cm ⁻¹) | Relative intensity | <i>ν</i> _{calc} ^a (cm ⁻¹) | <i>ν</i> _{obs} - <i>ν</i> _{calc} |
|--|-----------------|---|--------------------|---|--|
| 1-0 | R(40) | 20 486.7 | 10 ^b | 20 486.9 | -0.2 |
| 1-0 | P(42) | 20 364.8 | 10 | 20 364.9 | -0.1 |
| 1-1 | R(40) | 20 128.3 | 5 | 20 128.1 | 0.2 |
| 1-1 | P(42) | 20 007.5 | 4 | 20 007.5 | 0.0 |
| 1-2 | R(40) | 19 775.9 | 10 | 19 775.9 | 0.0 |
| 1-2 | P(42) | 19 656.8 | 8 | 19 656.8 | 0.0 |
| 1-3 | R(40) | 19 430.0 | 10 ^b | 19 429.9 | 0.1 |
| 1-3 | P(42) | 19 312.6 | 10 | 19 312.3 | 0.3 |
| 1-4 | R(40) | 19 090.4 | 20 | 19 090.6 | -0.2 |
| 1-4 | P(42) | 18 974.5 | 20 | 18 974.5 | 0.0 |
| 1-5 | R(40) | 18 757.2 | 15 | 18 757.7 | -0.5 |
| 1-5 | P(42) | 18 643.1 | 10 | 18 643.3 | -0.2 |
| 1-6 | R(40) | 18 430.9 | 8 | 18 431.4 | -0.5 |
| 1-6 | P(42) | 18 318.1 | 8 | 18 318.6 | -0.5 |
| 1-7 | R(40) | 18 111.1 | 5 | 18 111.8 | -0.7 |
| 1-7 | P(42) | 18 000.3 | 3 | 18 000.6 | -0.3 |

* With the molecular constants deduced in the course of this work (Table IV).

^b This fluorescence series has the remarkable property that it is excited

by two different laser lines. The intensity of a fluorescence line coincident with a laser line is measured using the other laser line for excitation.

series can be followed to high vibrational levels of the ground state, sometimes to nearly 80% of the dissociation energy of Li₂. This permits a spectroscopic determination of D_0^0 if we analyze the observed series to obtain rotational and vibrational constants which represent the levels involved. Then by a short Birge-Sponer extrapolation of the vibrational levels (with the rotational contribution removed), we can expect to determine a rather accurate value of the dissociation limit, and hence the dissociation energy of the $X^1\Sigma_g^+$ ground state.

The analysis consists of two parts. First it is necessary to determine the v'' , J'' levels of the fluorescence series, and then, with this knowledge, to obtain rotational and vibrational constants of the $X^1\Sigma_g^+$ state. A clue to the vibrational numbering can usually be obtained from the number of observed anti-Stokes fluorescence lines (lines with higher frequency than the exciting line). The fluorescence series in Table III is a case in point. This clue, however, can sometimes be misleading, especially if the initial v'' is rather large or if the series is weak. Under such conditions, the actual v'' may be larger than the number of anti-Stokes members observed.

In the analysis of a P - R series, the rotational numbering can be obtained from the spacings $\Delta_2 F_v(J'')$ within each P - R doublet, and $\Delta G_{v''+1/2}(J)$ within two successive P or R members of a series. In this step, the tentative v'' numbering, the molecular constants already available from the literature,²¹ and the relations

$$\Delta_2 F_v(J) = R(J-1) - P(J+1) = (4B_v - 6D_v)(J + \frac{1}{2}) - 8D_v(J + \frac{1}{2})^3 \quad (1)$$

and

$$\Delta G_{v+1/2}(J) = \Delta G_{v+1/2} + (B_{v+1} - B_v)J(J+1) \quad (2)$$

are used. Depending on the accuracy to which Eqs. (1) and (2) are satisfied, the tentative vibrational assignments can be confirmed or adjusted.

For Q series, where no immediate information about the magnitude of J is available, the correct v'' , J'' assignment may be quite difficult. Often, several v'' , J'' values can be assigned which would explain the observed lines almost equally well. If, for example, in a given assignment both v' and v'' are increased by one and simultaneously J is increased by about 10, the agreement between calculated and observed wavenumbers is practically unchanged, even for very long series. For the Q series the analysis can be facilitated by a special experimental procedure which produces P - R series with the same v' and v'' as the Q series in question. The analysis of these P - R series will then decide the numbering of the Q series in a definitive way.

The basis for this procedure is the fact that molecules in an excited (v' , J') state can be transferred by

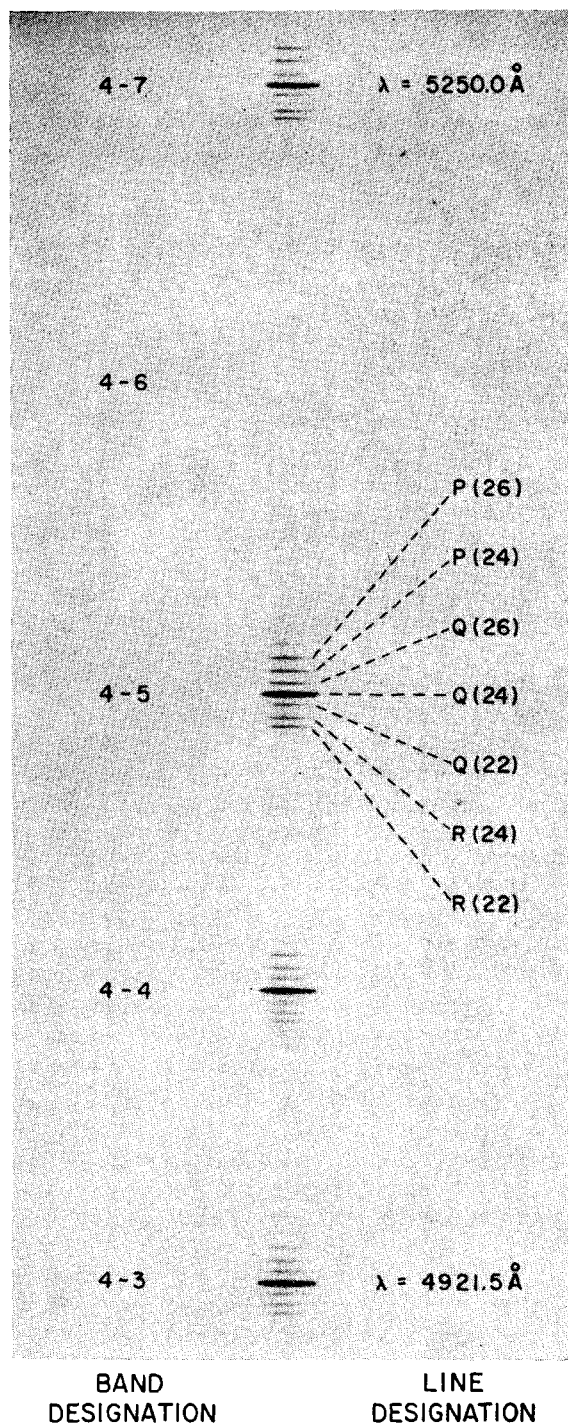


FIG. 1. Some members of the ${}^7\text{Li}_2$ $Q(24)$ fluorescence series showing satellite lines induced by collisions.

collisions into other rotational levels of the same v' state, from which they then emit fluorescence. In our experiments the collision partner was either the atomic Li vapor or Ar at a pressure of a few torr. Increasing the temperature to about 800–900°C sometimes was sufficient to produce the necessary amount of collisional gas. An excited level that was found to be

²¹ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1950).

TABLE IV. Molecular constants of the $X^1\Sigma_g^+$ state of ${}^7\text{Li}_2$, ${}^6\text{Li}^7\text{Li}$, and ${}^6\text{Li}_2$.

| Constant (cm^{-1}) | ${}^7\text{Li}_2^a$ Observed | ${}^6\text{Li}^7\text{Li}$ Observed | ${}^6\text{Li}^7\text{Li}^b$ Computed | ${}^6\text{Li}_2$ Observed | ${}^6\text{Li}_2^b$ Computed |
|----------------------------------|---------------------------------|--|--|-------------------------------|---------------------------------|
| B_e | 0.6726 | 0.717 | 0.729 | 0.7844 | 0.7845 |
| $\alpha_e \times 10^3$ | 6.8 | 8.4 | 7.7 | 8.3 | 8.6 |
| $\gamma_e \times 10^4$ | -1.0 | ... | ... | -1.3 | -1.4 |
| $D_e \times 10^6$ | 9.87 | (11.6) ^c | 11.6 | (13.43) ^c | 13.43 |
| $H_e \times 10^{10}$ | 1.54 | ... | ... | (2.45) ^c | 2.45 |
| ω_e | 351.43 | 365.6 | 365.78 | 378.72 | 379.54 |
| $\omega_e x_e$ | 2.610 | 2.74 | 2.83 | 2.985 | 3.044 |
| $\omega_e y_e \times 10^3$ | 2.95 | -13.8 | ... | 2.20 | 3.71 |
| $\omega_e z_e \times 10^4$ | -6.36 | ... | ... | -8.37 | -8.65 |

^a The rotational constants in this column are valid up to $v''=10$, ($B_{10}=0.5912$; $D_{10}=9.9 \times 10^{-8}$). At higher values of v'' , for which mainly series with $J > 35$ have been observed and analyzed, the effect of β_e is noticeable, and for these high vibrational levels, B_v and D_v are better represented by the expressions

$$B_v = B_{10} - 7.7 \times 10^{-4} (v-10) - 1.6 \times 10^{-4} (v-10)^2,$$

particularly sensitive to this collision-induced transfer was the $v'=4$, $J'=24$ level of ${}^7\text{Li}_2$. Its fluorescence was affected by collisions in the manner shown in Fig. 1, even at normal operating temperatures.

The interpretation of this pattern of lines is as follows. The main fluorescence consists of a Q series, which indicates that of the two Λ -doubling components of the $v'=4$, $J'=24$ level of the $B^1\Pi_u$ state only one was excited by the laser line (the lower one, because we are dealing with a ${}^1\Pi_u \rightarrow {}^1\Sigma_g^+$ transition²¹). Any collisional transfer from this state has to preserve the s or a symmetry, which is equivalent to preserving the parity²²; it will also lead predominantly to neighboring

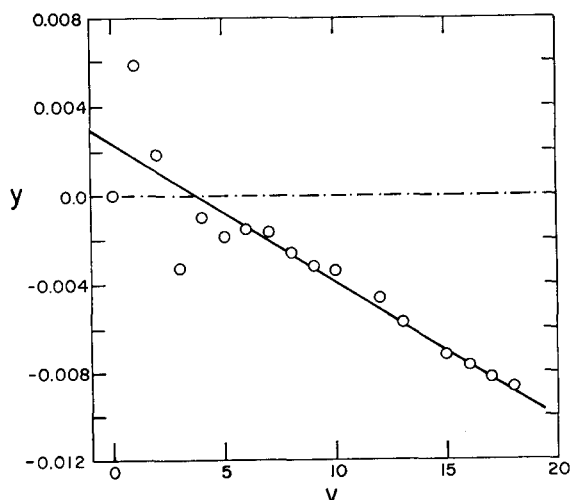


FIG. 2. Graphical representation of the function $y(v+\frac{1}{2}) = [G_v - \omega_e(v+\frac{1}{2}) + \omega_e x_e(v+\frac{1}{2})^2] / (v+\frac{1}{2})^3$. The G_v , ω_e , and $\omega_e x_e$ values are from our experimental data for ${}^7\text{Li}_2$ ($\omega_e=351.43 \text{ cm}^{-1}$ and $\omega_e x_e=2.610 \text{ cm}^{-1}$).

²² E. P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959). See also Ref. 21, pp. 130-132.

$$D_v = D_{10} + 2.2 \times 10^{-7} (v-10).$$

^b From isotopic relations: $\rho({}^6\text{Li}^7\text{Li}/{}^7\text{Li}_2) = 1.0408$; $\rho({}^6\text{Li}_2/{}^7\text{Li}_2) = 1.0800$.

^c The computed values have been used in the analysis of the experimental results.

states.²³ The upper Λ component of a rotational level J has the same parity as the lower components of the $J \pm 1$, $J \pm 3$, $J \pm 5$, ... levels, and also the same parity as the upper components of the $J \pm 2$, $J \pm 4$, $J \pm 6$, ... levels. Thus, the states most likely to be populated by collisions from the $J'=24$ sublevel excited by the laser line are the upper Λ components of the neighboring levels $J'=23$ and $J'=25$ of $v'=4$. From both of these levels, P - R fluorescence series are emitted. Therefore,

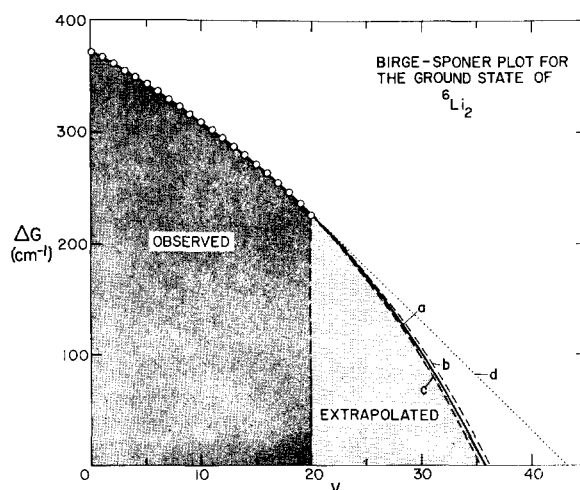


FIG. 3. Vibrational quanta ($\Delta G_{v+1/2}$) as a function of v in the $X^1\Sigma_g^+$ state of ${}^6\text{Li}_2$: (a) with the interpretation given in the text; (b, c) extreme alternative interpretations in agreement with our observed G_v data; (d) extrapolation required to obtain a value of $D_0^0=1.14 \text{ eV}$, which was previously suggested to be the correct dissociation energy. The dissociation energy is given by the area under the $\Delta G_{v+1/2}$ curve. The dark-shaded portion corresponds to observed levels and represents almost 80% of the dissociation energy.

²³ See, for example: H. P. Broida and T. Carrington, *J. Chem. Phys.* **38**, 136 (1963); R. L. Brown and W. Klemperer, *ibid.* **41**, 3072 (1964); J. I. Steinfeld and W. Klemperer, *ibid.* **42**, 3475 (1965).

TABLE V. The ⁶Li₂ fluorescence progression (11, 29→*v*'', 28-30), *E*' = 23 645.1 cm⁻¹.

| <i>v</i> '' | Line | <i>v</i> (cm ⁻¹) | <i>G_v</i> (obs) (cm ⁻¹) | <i>G_v</i> (calc) (cm ⁻¹) | <i>G_v</i> (obs) - <i>G_v</i> (calc) |
|-------------|-------|---------------------------------|---|--|---|
| 2 | R(28) | 22 106.4 | 928.2 | 928.1 | 0.1 |
| | P(30) | ... | ... | | ... |
| 3 | R(28) | 21 753.1 | 1288.8 | 1288.9 | -0.1 |
| | P(30) | 21 666.9 | 1288.8 | | -0.1 |
| 4 | R(28) | 21 405.9 | 1643.7 | 1643.7 | 0.0 |
| | P(30) | 21 320.8 | 1643.6 | | -0.1 |
| 5 | R(28) | 21 064.9 | 1992.4 | 1992.3 | 0.1 |
| | P(30) | 20 981.1 | 1992.2 | | -0.1 |
| 6 | R(28) | ... | ... | 2334.7 | ... |
| | P(30) | ... | ... | | ... |
| 7 | R(28) | 20 402.5 | 2670.9 | 2670.8 | 0.1 |
| | P(30) | 20 320.9 | 2670.8 | | 0.0 |
| 8 | R(28) | 20 081.3 | 3000.7 | 3000.4 | 0.3 |
| | P(30) | 20 001.2 | 3000.3 | | -0.1 |
| 9 | R(28) | 19 767.2 | 3323.4 | 3323.5 | -0.1 |
| | P(30) | 19 687.8 | 3323.6 | | 0.1 |
| 10 | R(28) | 19 459.9 | 3639.5 | 3639.8 | -0.3 |
| | P(30) | 19 382.0 | 3639.5 | | -0.3 |
| 11 | R(28) | ... | ... | 3949.2 | ... |
| | P(30) | ... | ... | | ... |
| 12 | R(28) | 18 866.5 | 4251.2 | 4251.4 | -0.2 |
| | P(30) | 18 791.2 | 4251.1 | | -0.3 |
| 13 | R(28) | 18 581.3 | 4545.9 | 4546.3 | -0.4 |
| | P(30) | ... | ... | | ... |
| 14 | R(28) | ... | ... | 4833.5 | ... |
| | P(30) | 18 231.5 | 4832.9 | | -0.6 |
| 15 | R(28) | 18 034.3 | 5112.4 | 5112.9 | -0.4 |
| | P(30) | 17 963.3 | 5112.3 | | -0.6 |
| 16 | R(28) | ... | ... | 5384.0 | ... |
| | P(30) | ... | ... | | ... |
| 17 | R(28) | 17 520.2 | 5646.9 | 5646.7 | 0.2 |
| | P(30) | 17 452.6 | 5646.5 | | -0.2 |
| 18 | R(28) | 17 277.0 | 5900.6 | 5900.5 | 0.1 |
| | P(30) | 17 210.8 | 5900.3 | | -0.2 |
| 19 | R(28) | 17 042.5 | 6145.4 | 6145.3 | 0.1 |
| | P(30) | 16 978.1 | 6145.2 | | -0.1 |
| 20 | R(28) | ... | ... | 6380.5 | ... |
| | P(30) | 16 755.2 | 6380.7 | | 0.2 |
| 21 | R(28) | 16 603.5 | 6606.9 | 6605.7 | 1.2 |
| | P(30) | 16 543.1 | 6605.5 | | -0.2 |

TABLE VI. The ${}^6\text{Li}_2$ fluorescence progression (9, 31 \rightarrow v'', 31), $E' = 23\,350.11\text{ cm}^{-1}$.

| v'' | Line | ν (cm^{-1}) | G_v (obs) (cm^{-1}) | G_v (calc) (cm^{-1}) | G_v (obs) - G_v (calc) |
|-------|-------|-------------------------------|-------------------------------------|--------------------------------------|-------------------------------|
| 2 | Q(31) | 21 679.1 | 928.5 | 928.1 | 0.4 |
| 3 | Q(31) | 21 326.6 | 1289.0 | 1288.9 | 0.1 |
| 4 | Q(31) | 20 981.1 | 1643.8 | 1643.7 | 0.1 |
| 5 | ... | ... | ... | 1992.3 | ... |
| 6 | Q(31) | 20 309.3 | 2334.8 | 2334.7 | 0.1 |
| 7 | Q(31) | 19 983.1 | 2671.0 | 2670.8 | 0.2 |
| 8 | Q(31) | 19 663.6 | 3000.9 | 3000.4 | 0.5 |
| 9 | Q(31) | 19 351.3 | 3323.7 | 3323.5 | 0.2 |
| 10 | Q(31) | 19 046.5 | 3639.3 | 3639.8 | -0.5 |
| 11 | Q(31) | 18 747.3 | 3949.5 | 3949.2 | 0.3 |
| 12 | Q(31) | 18 456.6 | 4251.5 | 4251.5 | 0.0 |
| 13 | Q(31) | 18 173.5 | 4546.2 | 4546.3 | -0.1 |
| 14 | Q(31) | 17 898.2 | 4833.4 | 4833.6 | -0.2 |
| 15 | Q(31) | 17 631.0 | 5112.5 | 5112.9 | -0.4 |
| 16 | Q(31) | 17 372.4 | 5383.5 | 5384.0 | -0.5 |
| 17 | Q(31) | 17 122.0 | 5646.5 | 5646.7 | -0.2 |
| 18 | Q(31) | 16 880.8 | 5900.5 | 5900.5 | 0.0 |
| 19 | Q(31) | 16 649.2 | 6145.2 | 6145.3 | -0.1 |

under the influence of collisions, each main Q line gives rise to two rather strong P - R doublets, and this accounts for four of the satellites around each Q line in Fig. 1. From the $\Delta_2 F_v(J)$ within each of these doublets we can easily find the J' value (23 and 25, respectively) which determines unambiguously that J' is 24 for the Q series. Two other strong satellites originate from collisional transfer with $\Delta J = \pm 2$, leading to the lower Λ components of the $J' = 22$ and $J' = 26$ rotational levels, and giving rise to a Q line on either side. Transitions with $\Delta J > 2$ are also observed but are weaker.

Similar satellites have been found in cases where the original lines are P - R doublets. Here, $\Delta J = \pm 1$ leads to the emission of two Q satellites appearing slightly to the right and to the left of the midpoint of the original P - R doublet. Transitions with $\Delta J = \pm 2$ cause, in turn, two new pairs of P - R lines.

Knowing the vibrational and rotational numbering of the lines observed, the determination of molecular constants of the ground state can be made by means of the combination relations among rotational lines.

In general, the rotational levels of a molecular state with $\Lambda = 0$ can be expressed in the form

$$F_v(J) = [B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \dots] J(J+1) - [D_e + \beta_e(v + \frac{1}{2}) + \dots] J^2(J+1)^2 + [H_e + \epsilon_e(v + \frac{1}{2}) + \dots] J^3(J+1)^3 + \dots \quad (3)$$

Ignoring the term with $J^3(J+1)^3$, we obtain from the preceding expression

$$\Delta_2 F_v(J) / (4J+2) = [(B_e - \frac{1}{2}\alpha_e + \frac{1}{4}\gamma_e) - (2J^2 + 2J + 2)(D_e + \frac{1}{2}\beta_e) - [\alpha_e - \gamma_e - (2J^2 + 2J + 2)\beta_e]v + \gamma_e v^2, \quad (4)$$

where $\Delta_2 F_v(J) = F_v(J+1) - F_v(J-1)$ is the wave-number difference between a pair of P and R lines

arising from a common upper level J , and all the constants refer to the ground state.

In (4) the two coefficients in the first bracket are just the rotational constants B_0 and D_0 of the $v'' = 0$ vibrational level:

$$B_e - \frac{1}{2}\alpha_e + \frac{1}{4}\gamma_e = B_0 \quad \text{and} \quad D_e + \frac{1}{2}\beta_e = D_0. \quad (5)$$

B_0 and D_0 can be taken from absorption measurements²⁴ on Li_2 which, for low values of v'' , yield very accurate ground-state rotational constants. In the case of ${}^6\text{Li}_2$, for which no absorption data are available, B_0 and D_0 were calculated using the well-known isotopic relations.²¹

This gives

$$\Delta_2 F_v(J) / (4J+2) = [B_0 - (2J^2 + 2J + 2)D_0] - [\alpha_e - \gamma_e + (2J^2 + 2J + 2)\beta_e]v + \gamma_e v^2, \quad (6)$$

which for simplicity we may write

$$f = a - bv + cv^2. \quad (7)$$

For each P - R series " a " is a known quantity, and a plot of

$$(f-a)/v = -b + cv \quad (8)$$

yields values of " b " and $c \equiv \gamma_e$ for each P - R series. The γ_e values are averaged, and then α_e and β_e can be obtained from plots of the J dependence of b :

$$b = \alpha_e - \gamma_e + (2J^2 + 2J + 2)\beta_e. \quad (9)$$

For $J > 35$ the effect of the terms with $J^3(J+1)^3$ in (3) can no longer be ignored. Therefore, a term $H_v J^3(J+1)^3$ is subtracted from the experimental value of $F_v(J)$, where the value of $H_v \approx H_e$ is again obtained from ab-

²⁴ A. McKellar and F. A. Jenkins, Publ. Dominion Astrophys. Observatory, Victoria, B.C. 7, 155 (1939).

TABLE VII. The ⁷Li₂ fluorescence progression (9, 38→*v*'', 37-39), *E*' = 23 354.93 cm⁻¹.

| <i>v</i> '' | Line | <i>ν</i> (cm ⁻¹) | <i>G_v</i> (obs) (cm ⁻¹) | <i>G_v</i> (calc) (cm ⁻¹) | <i>G_v</i> (obs) - <i>G_v</i> (calc) |
|-------------|-------|---------------------------------|---|--|---|
| 3 | R(37) | 21 265.1 | 1198.1 | 1198.1 | 0.0 |
| | P(39) | 21 169.8 | 1197.9 | | -0.2 |
| 4 | R(37) | 20 945.0 | 1528.0 | 1528.6 | -0.6 |
| | P(39) | 20 850.8 | 1528.0 | | -0.6 |
| 5 | R(37) | ... | ... | 1853.8 | ... |
| | P(39) | ... | ... | | ... |
| 6 | R(37) | 20 321.8 | 2173.2 | 2173.7 | -0.5 |
| | P(39) | 20 230.3 | 2172.7 | | -1.0 |
| 7 | R(37) | ... | ... | 2488.2 | ... |
| | P(39) | ... | ... | | ... |
| 8 | R(37) | 19 720.5 | 2797.5 | 2797.1 | 0.4 |
| | P(39) | 19 631.2 | 2797.4 | | 0.3 |
| 9 | R(37) | 19 429.7 | 3100.3 | 3100.4 | -0.1 |
| | P(39) | 19 340.9 | 3100.9 | | 0.5 |
| 10 | R(37) | 19 143.4 | 3398.8 | 3397.9 | 0.9 |
| | P(39) | 19 056.7 | 3398.7 | | 0.8 |
| 11 | R(37) | ... | ... | 3686.6 | ... |
| | P(39) | ... | ... | | ... |
| 12 | R(37) | 18 591.0 | 3976.0 | 3975.3 | 0.7 |
| | P(39) | 18 507.3 | 3976.0 | | 0.7 |
| 13 | R(37) | 18 324.1 | 4253.7 | 4254.8 | -1.1 |
| | P(39) | 18 241.2 | 4253.8 | | -1.0 |
| 14 | R(37) | ... | ... | 4527.9 | ... |
| | P(39) | ... | ... | | ... |
| 15 | R(37) | 17 810.8 | 4793.5 | 4794.4 | -0.9 |
| | P(39) | 17 731.1 | 4793.5 | | -0.9 |
| 16 | R(37) | 17 564.7 | 5053.9 | 5054.2 | -0.3 |
| | P(39) | 17 486.6 | 5053.9 | | -0.3 |
| 17 | R(37) | 17 325.7 | 5306.8 | 5306.9 | -0.1 |
| | P(39) | 17 249.1 | 5306.8 | | -0.1 |
| 18 | R(37) | 17 094.1 | 5552.9 | 5552.4 | 0.5 |
| | P(39) | 17 019.3 | 5552.9 | | 0.5 |

sorption data. Then $\Delta_2 F_v(J)$ is treated in the manner described above.

With this method of analysis it was found that in each molecular species the parameter "*b*" was practically the same for all series, implying that the correction due to β_0 was really very small.

For most vibrational levels with $v'' > 8$, only one *P-R* doublet and one or two *Q* lines are observed for each value of v'' . To analyze these series it is necessary to use both *P-R* and *Q* lines. From a knowledge of the molecular constants of the low v'' states it is possible to determine the energies, E' , of the upper levels to

TABLE VIII. The ${}^7\text{Li}_2$ fluorescence progression ($7, 61 \rightarrow v'', 61$), $E' = 24\,116.88\text{ cm}^{-1}$.

| v'' | Line | ν (cm^{-1}) | G_v (obs) (cm^{-1}) | G_v (calc) (cm^{-1}) | G_v (obs) - G_v (calc) |
|-------|---------|-------------------------------|-------------------------------------|--------------------------------------|-------------------------------|
| 2 | $Q(61)$ | 20 909.5 | 862.3 | 862.3 | 0.0 |
| 3 | $Q(61)$ | 20 601.8 | 1197.6 | 1198.1 | -0.5 |
| 4 | $Q(61)$ | ... | ... | 1528.6 | ... |
| 5 | $Q(61)$ | 20 004.1 | 1852.8 | 1853.8 | -1.0 |
| 6 | $Q(61)$ | 19 713.4 | 2173.4 | 2173.7 | -0.3 |
| 7 | $Q(61)$ | 19 429.7 | 2487.7 | 2488.2 | -0.5 |
| 8 | $Q(61)$ | 19 151.2 | 2797.6 | 2797.1 | 0.5 |
| 9 | $Q(61)$ | 18 880.3 | 3100.7 | 3100.4 | 0.3 |
| 10 | $Q(61)$ | ... | ... | 3398.0 | ... |
| 11 | $Q(61)$ | 18 356.2 | 3690.3 | 3689.8 | 0.5 |
| 12 | $Q(61)$ | 18 105.4 | 3975.6 | 3975.3 | 0.3 |
| 13 | $Q(61)$ | ... | ... | 4254.8 | ... |
| 14 | $Q(61)$ | 17 624.4 | 4528.7 | 4527.9 | 0.8 |
| 15 | $Q(61)$ | 17 395.6 | 4793.5 | 4794.4 | -0.9 |
| 16 | $Q(61)$ | 17 174.7 | 5053.4 | 5054.2 | -0.8 |
| 17 | $Q(61)$ | 16 962.0 | 5306.4 | 5306.9 | -0.5 |
| 18 | $Q(61)$ | 16 758.4 | 5552.6 | 5552.4 | 0.3 |

which the molecule was excited by the laser line (ν_L):

$$E' = E'' + \nu_L = G_{v''} + B_{v''}J(J+1) - D_{v''}J^2(J+1)^2 + H_{v''}J^3(J+1)^3 + \nu_L. \quad (10)$$

It is then possible to formulate a relation among the lines by which not only P and R lines, but also Q lines can be used to determine rotational constants for each vibrational level of the ground state.

The differences $(E_1' - E_2') - (\nu_1 - \nu_2)$, corresponding to any pair of lines, is always $F_v(J_1) - F_v(J_2)$, the difference between the rotational energies of the levels of the ground state. This difference may be written

$$\begin{aligned} F_v(J_1) - F_v(J_2) &= (E_1' - E_2') - (\nu_1 - \nu_2) \\ &= B_v[J_1(J_1+1) - J_2(J_2+1)] \\ &\quad - D_v[J_1^2(J_1+1)^2 - J_2^2(J_2+1)^2] \\ &\quad + H_v[J_1^3(J_1+1)^3 - J_2^3(J_2+1)^3], \quad (11) \end{aligned}$$

and hence, assuming $H_v = H_e$ for all v'' levels,

$$\begin{aligned} \frac{(E_1' - E_2') - (\nu_1 - \nu_2) - H_e[J_1^3(J_1+1)^3 - J_2^3(J_2+1)^3]}{J_1(J_1+1) - J_2(J_2+1)} \\ = B_v - D_v[J_1(J_1+1) + J_2(J_2+1)], \quad (12) \end{aligned}$$

from which B_v and D_v can be easily determined for each vibrational level. Note that as few as three line positions yield already three energy differences, from which the rotational constants B_v and D_v can be obtained.

Alternatively, the constants B_e , α_e , γ_e , D_e , and H_e found from the analysis of the first nine vibrational levels can be used to determine the B_v and D_v corresponding to each vibrational level with $v'' > 8$, and with these extrapolated B_v and D_v values the energy of the vibrational energy levels ($v'' > 8$) could be found from the observed line positions. For series with $J < 35$

these methods produced similar results. In particular, the dissociation limits obtained from the two sets of vibrational energy levels were practically identical. The ${}^6\text{Li}_2$ results presented below are based on the rotational constants B_e , D_e , α_e , and γ_e obtained from the first nine v'' levels of this molecule. For ${}^7\text{Li}_2$, where series with $J > 35$ have been analyzed up to high v'' levels, the effect of small changes in the rotational constants is more important, which makes it necessary to use the individual B_v and D_v constants obtained directly from the observed lines and relation (12). The observed ${}^6\text{Li}{}^7\text{Li}$ series were not long enough to use in the determination of the dissociation limit. For this molecule, only constants representing the observed lines have been deduced from the experimental data.

From the G_v values obtained as a result of the rotational analysis we find the vibrational constants of the well-known expression

$$G_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 + \dots \quad (13)$$

The constants ω_e and $\omega_e x_e$ are deduced from the first vibrational levels on which the effect of the $\omega_e y_e$ and $\omega_e z_e$ is negligible. Then, representing

$$[G_v - \omega_e(v + \frac{1}{2}) + \omega_e x_e(v + \frac{1}{2})^2] / (v + \frac{1}{2})^3 \quad (14)$$

as a function of $(v + \frac{1}{2})$, a straight line is obtained whose intercept is $\omega_e y_e$ and whose slope is $\omega_e z_e$ (see Fig. 2). The fact that the data points in Fig. 2 are fit by a straight line for high v'' demonstrates that higher terms in the G_v expansion can be neglected. A term $\omega_e t_e(v + \frac{1}{2})^5$ with $\omega_e t_e = 10^{-6}$ would produce a noticeable curvature in that kind of plot but would only mean a change of about 0.01 eV in the dissociation limit. Therefore we assume that the terms in expression (13) are sufficient to describe the vibrational

structure of the ground state of Li_2 . Equation (14) is used to compute $\omega_e y_e$ and $\omega_e z_e$ from the observed data.

Table IV is a summary of all the molecular constants deduced from this analysis. In columns 4 and 6 the values of the ${}^6\text{Li}^7\text{Li}$ and ${}^6\text{Li}_2$ constants, obtained by applying the corresponding isotopic factors to the ${}^7\text{Li}_2$ constants, are also presented. The good agreement between these "predicted" and observed constants is a confirmation of the correctness of the analysis.

Tables V–VIII contain some of the long series studied, with a comparison between the calculated and observed vibrational energy levels (G_v). These comparisons give a general idea about the accuracy of our results.

Using the vibrational constants given in Table IV the vibrational energy levels have been extrapolated to G_{max} , the dissociation limit of the ground state.²⁵ We obtain for the energy D_e , measured from the bottom of the potential well, the mean value $8460 \pm 50 \text{ cm}^{-1}$ for ${}^7\text{Li}_2$ and $8440 \pm 50 \text{ cm}^{-1}$ for ${}^6\text{Li}_2$. According to theory these two values must be practically equal for both isotopic species.²⁶ Therefore we may accept the value $8450 \pm 50 \text{ cm}^{-1}$ as the dissociation limit (D_e) of the $X^1\Sigma_g^+$ state of Li_2 . In the particular case of ${}^7\text{Li}_2$, to obtain the dissociation energy D_0^0 , measured from $v''=0$, we must subtract the zero-point energy of this molecule (175 cm^{-1}). We then obtain the value $D_0^0({}^7\text{Li}_2) = 8275 \pm 50 \text{ cm}^{-1}$ corresponding to $1.026 \pm 0.006 \text{ eV}$, or $23.66 \pm 0.14 \text{ kcal/mole}$.

To assess the accuracy of our value for the dissociation energy, we have tried several other ways of analyzing the experimental results. They differ in two respects. First, we have used different rotational constants to obtain the vibrational levels, such as the constants quoted by Herzberg,²¹ the constants derived from Eq. (12), or extrapolated from those obtained for $v'' < 8$. Second, each set of vibrational energy levels has been expressed in different power series of $v + \frac{1}{2}$ compatible with our experimental accuracy. The calculated D_0^0 for all these alternative procedures is within $\pm 50 \text{ cm}^{-1}$ of the value given above. The Birge–Sponer plot in Fig. 3 illustrates this point for the case of ${}^6\text{Li}_2$.

DISCUSSION

The present result supports the value of D_0^0 obtained by Lewis⁵ and therefore confirms the existence of a hump in the potential curve of the $B^1\Pi_u$ state of Li_2 .

To our value of D_0^0 , we add the energy of the $2p^2P$ level of the Li atom,²⁷ 14904 cm^{-1} , and arrive at $23179 \pm 50 \text{ cm}^{-1}$ for the energy of two separated Li atoms, one of them excited. This energy is referred to the $v''=0$ level of the ${}^7\text{Li}_2$ ground state. If, on the other

hand, we add Loomis and Nusbaum's dissociation energy for the $B^1\Pi_u$ state, $D_0 = 3711 \pm 240 \text{ cm}^{-1}$, to the band system origin $\nu_{00} = 20396 \text{ cm}^{-1}$, we arrive at $24107 \pm 240 \text{ cm}^{-1}$ using the same reference energy level. The difference of $928 \pm 300 \text{ cm}^{-1}$ represents the height of the potential hump, corresponding to $0.12 \pm 0.04 \text{ eV}$ or $2.8 \pm 0.9 \text{ kcal/mole}$. Note that in general Birge–Sponer extrapolations tend to overestimate the dissociation energy. Thus the possible effect of higher-order terms in the expansion of $G(v)$ in powers of $(v + \frac{1}{2})$ would only increase the magnitude of the hump. This hump is a major feature of the $\text{Li}_2 B^1\Pi_u$ potential curve, representing about 35% of the total binding energy of this state.

Potential humps can arise from three different sources. The first and perhaps best known is an avoided curve crossing between two potentials of the same symmetry, one repulsive and one attractive.²¹ A second is what may be called a first-order dispersion energy, or excitation-exchange energy. This can occur only for homonuclear diatomics and was the basis of King and Van Vleck's prediction¹⁰ that the lowest-lying ${}^1\Pi_u$ excited states of the alkali dimers would have a potential maximum. If the energy states of the separated atoms are connected by a dipole transition, the leading term of the first-order dispersion energy will be proportional to R^{-3} . For ${}^1\Pi_u$ states formed from two identical atoms, one in a 2S state and one in a ${}^2P^0$ state, King and Van Vleck showed that the first-order dispersion energy was repulsive, and hence leads to a potential hump if the ${}^1\Pi_u$ state is bound. The third type of interaction which can produce a potential hump is the change of the valence-type forces (chemical forces arising from electron exchange) with internuclear separation. This interaction has not been thoroughly studied at intermediate internuclear separations. Work by Buckingham and Dalgarno²⁸ and by Rosen and Ikehara²⁹ provides examples of this type of potential barrier.

Recently, Mulliken³⁰ has presented a general discussion of the interaction of differently excited like atoms at intermediate to large distances. He has shown that in many cases all three mechanisms can be operative and the decision as to the origin and magnitude of the hump must await detailed quantum-mechanical calculations. For the $B^1\Pi_u$ state of the Li_2 molecule the first-order dispersion energy will certainly contribute to the observed potential barrier, but may not be the only important factor. An avoided curve crossing with $\text{Li}^+ + \text{Li}^{-*}$ (where by Li^{-*} we mean an excited virtual state of Li^- which becomes stabilized on approaching Li^+) must be considered. The possibility

²⁸ R. A. Buckingham and A. Dalgarno, Proc. Roy. Soc. (London) **A213**, 327 (1952).

²⁹ N. Rosen and S. Ikehara, Phys. Rev. **43**, 5 (1933); N. Rosen, *ibid.* **43**, 671 (1933).

³⁰ R. S. Mulliken, Phys. Rev. **120**, 1674 (1960).

²⁵ Since there is no theoretical reason to expect a hump in the ground-state potential curve, we have taken G_{max} equal to D_e .

²⁶ P. R. Bunker, J. Mol. Spectry. **28**, 422 (1968).

²⁷ C. M. Sitterly, Natl. Bur. Std. (U.S.) Circ. **467** (1949).

that overlap forces contribute to the formation of the potential hump also must be taken into account. The height of the potential maximum will depend critically on the interaction. We hope that our experimental determination of the magnitude of the potential barrier will encourage a full theoretical treatment to elucidate

the relative contributions of the three different interactions we have described.

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Optical Pumping of Molecules*

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A technique is described for the optical pumping of gas-phase molecules based on the orientation dependence of their absorption cross section. It is shown that when the rate of excitation exceeds the relaxation rate of a ground-state (v'' , J'') level, the magnetic sublevels are preferentially "burned away" and the steady-state M -level population is altered appreciably. An experiment to demonstrate molecular alignment has proved successful using the 4880-Å line of a cw argon-ion laser to cause the transition ($v''=3$, $J''=43$) \rightarrow ($v'=6$, $J'=43$) in the $B^1\Pi_u - X^1\Sigma_g^+$ blue-green band system of the Na_2 molecule. The establishment of an unequal magnetic sublevel population is detected by monitoring the degree of polarization P of the fluorescence as a function of laser intensity. It is found that P first remains constant then decreases by about 50% as the laser-beam power increases from 0.1 to 150 mW. In addition, the absorption becomes nonlinear with a power threshold corresponding to the onset of the decrease in P . This optical pumping technique is applicable to a wide class of molecules, and both simple classical and quantum mechanical theories of the pumping process have been formulated. These theories relate the degree of polarization to both the pumping rate and the relaxation time of the pumped level. The time-dependent as well as steady-state behavior of P is examined. Under conditions of strong optical pumping it is predicted that the degree of polarization as a function of time will overshoot its steady-state value, and as the pumping rate increases large negative transients in P will appear.

I. INTRODUCTION

In 1950, Kastler¹ proposed a method for altering the relative population of the Zeeman levels or hyperfine levels of ground state atoms with optical irradiation. He visualized a two-step process whereby atoms in sublevel A are raised to the excited state B from which they decay by spontaneous emission back to A or to a new sublevel C (See Fig. 1). If the rate of depopulation of C to A by relaxation (through collisional or radiative means) is slower than the rate of population of C , then level C becomes appreciably populated at the expense of level A and the atomic system is said to be optically pumped. Successful optical pumping experiments were first carried out on the ^{23}Na ground state in a beam by Brossel, Kastler, and Winter² and by Hawkins and

Dicke,³ and in a bulb by Margerie,⁴ by Bender,⁵ and by Hartmann, Rambosson, Brossel, and Kastler.⁶

Since these early experiments a number of attempts have been made to achieve optical pumping in other atomic systems and these investigations have led to very accurate determinations of atomic magnetic moments, hyperfine interactions, pressure shifts, light shifts, disorientation cross sections, diffusion constants, and other quantities.⁷ However, almost without exception,⁸ it has been found that only in atomic S states does the spin orientation persist for a sufficient length of

³ W. B. Hawkins and R. H. Dicke, *Phys. Rev.* **91**, 1008 (1953).

⁴ J. Margerie, *Compt. Rend.* **241**, 865 (1955).

⁵ P. L. Bender, thesis, Princeton University, Princeton, N.J., 1956 (unpublished).

⁶ F. Hartmann, M. Rambosson, J. Brossel, and A. Kastler, *Compt. Rend.* **246**, 1522 (1958).

⁷ For a review see R. A. Bernheim, *Optical Pumping: An Introduction* (W. A. Benjamin, Inc., New York, 1965) and C. Cohen-Tannoudji and A. Kastler in *Progress in Optics*, E. Wolf, Ed. (North-Holland Publ. Co., Amsterdam, 1966), Vol. 5, pp. 3-81.

⁸ Recently, L. D. Scheerer [*Phys. Rev. Letters* **21**, 660 (1968); *Phys. Rev.* **180**, 83 (1969)] has succeeded in optically pumping metastable Ne (3P_2) atoms as well as other rare-gas metastable atoms (private communication) having an outer s electron and an inner p electron hole. See also H. M. Gibbs, B. Chang, and R. C. Greenhow, *Phys. Rev. Letters* **22**, 270 (1969).

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¹ A. Kastler, *J. Phys. Radium* **11**, 225 (1950).

² J. Brossel, A. Kastler, and J. Winter, *J. Phys. Radium* **13**, 668 (1952).