

Some Propensity Rules in Collision-Induced Rotational Quantum Jumps*

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When a mixture of lithium vapor and argon is irradiated with the light from an argon ion laser and the resulting fluorescence of the $\text{Li}_2 B {}^1\Pi_u-X {}^1\Sigma_g^+$ band system is examined under high resolution, a pattern of collision-induced satellite lines is observed to accompany the parent resonance fluorescence series. Under conditions of low pressure these satellite lines originate from single inelastic events which alter the rotational state of the excited Li_2 molecule. The relative intensities of the satellite lines are found to be markedly different depending on whether the collision-induced transition originates from the upper or lower component of the Λ doublet of the Π state, referred to as c or d , respectively. An increase in J ($+\Delta J$ jump) is favored over a decrease ($-\Delta J$) for $d \rightarrow c$ jumps whereas $-\Delta J$ is favored over $+\Delta J$ for $c \rightarrow d$ jumps. On the other hand $\pm\Delta J$ changes that preserve the character of the Λ component, i.e., $c \rightarrow c$ and $d \rightarrow d$, occur with nearly equal probability for the same value of ΔJ . This behavior has been observed for the satellite lines corresponding to $\Delta J = \pm 1, \pm 2$, and in some cases ± 3 for (v', J', c , or d) levels (2, 31, c), (3, 30, c), (9, 38, c), (4, 24, d), and (7, 61, d) of ${}^7\text{Li}_2$ and (0, 45, d) of ${}^6\text{Li } {}^7\text{Li}$. In ${}^7\text{Li}_2$ only collisional transitions between symmetric or between antisymmetric levels are allowed. For ${}^6\text{Li } {}^7\text{Li}$, which does not have this symmetry, more satellite lines are observed. However, these additional lines are significantly weaker since the ${}^6\text{Li } {}^7\text{Li}$ molecule is nearly homonuclear. A simple classical model is suggested which may help to explain the different rotational quantum jump propensities for the two Λ components.

INTRODUCTION

Resonance fluorescence of molecules excited by monochromatic radiation is a well-established method for obtaining information about the rotational relaxation of electronically excited states.¹ In this technique a foreign gas is added that changes the rotational state of the excited molecule causing the appearance of satellite lines. By measuring the rate of growth of these satellites, rotational transfer cross sections can be determined, provided the radiative lifetime of the molecular excited state and the quenching cross section are known. The relative intensities of the satellite lines can provide information about the tendency or propensity of a certain molecule to undergo a ΔJ change of a given magnitude and sign. Some notable applications of this technique are the recent investigations of rotational energy transfer in the $A {}^2\Sigma^+$ state of OH,² the $A {}^2\Sigma^+$ state of NO,³ the $B {}^3\Pi_{0+2}$ state of I_2 ,⁴ and the $B {}^1\Sigma_u^+$ state of HD.⁵ In general, these experiments have shown that ΔJ changes have gas kinetic cross sections and that a given ΔJ change drops off slowly with increasing ΔJ , provided the rotational energy transfer is not larger than the thermal energy. It has also been found that the change in J by more than one quantum can be effected by a single collision. Furthermore, the probability for an increase in J by ΔJ has been observed to be nearly equal to the probability for a decrease by the same ΔJ , usually with some preference towards the equilibrium state.

In a previous paper,⁶ hereafter referred to as I, we described the excitation of eleven fluorescence series of the $\text{Li}_2 B {}^1\Pi_u-X {}^1\Sigma_g^+$ band system by the lines of a cw argon ion laser. We report here a detailed investigation of individual rotational inelastic collisions which the excited Li_2 molecule undergoes with argon atoms. This

represents the first study of collision-induced rotational transitions in a ${}^1\Pi$ electronic state. The results show that a ${}^1\Pi$ state behaves quite differently from the previous cases studied. In particular, if the collision changes J by one quantum, there is a strong propensity for an increase or decrease in J depending on the component of the Λ doublet which is initially populated. So far this behavior has been observed only for the $B {}^1\Pi_g$ state of ${}^7\text{Li}_2$ and ${}^6\text{Li } {}^7\text{Li}$. However, we shall present a classical model for this effect which indicates that the two Λ components of an electronically degenerate state will possess, in general, different rotational transfer properties.

EXPERIMENTAL

The experimental setup was the same as that used in I. Light from a cw argon-ion laser was incident upon lithium vapor contained in a T -shaped fluorescence cell. For this experiment the pressure in the cell could be controlled. A mechanical pump (50 liter/min) evacuated the cell through a liquid nitrogen trap to a pressure of the order of 10^{-3} torr at the operating temperature of 650°C . Under these conditions no satellites were seen around the fluorescence lines (with a detection limit of about 0.1% of the intensity of the more prominent fluorescence lines). Then argon gas (AirCo Research grade purity 99.9995%) was added at pressures ranging from 15–0.15 torr as measured by an Autovac Pirani gauge. The pressure calibration may be in error by 50%; however, knowledge of the absolute pressure is unimportant in this work. The vicinity of certain selected fluorescence lines was scanned photoelectrically for collision-induced satellites using a $\frac{3}{4}$ -m SPEX spectrometer.

All fluorescence lines are not equally suitable for this experiment. They should fulfill the following require-

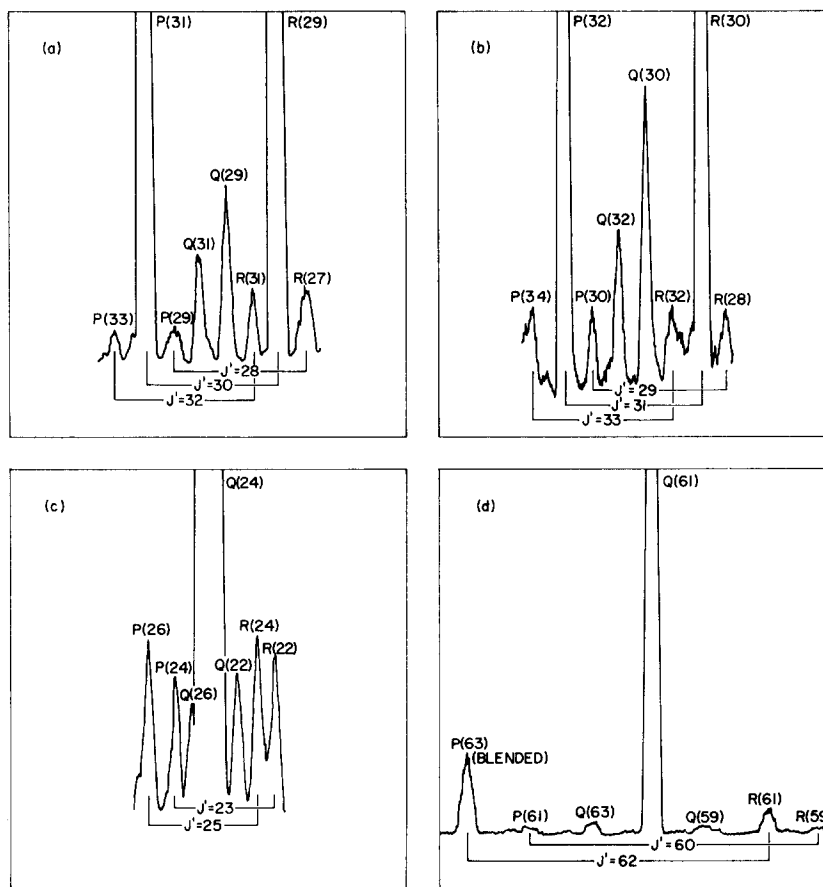


FIG. 1. Collision-induced satellite patterns accompanying the fluorescence resulting from the excitation of (a) the ($v'=3$, $J'=30$, c) level, (b) the ($v'=2$, $J'=31$, c) level, (c) the ($v'=4$, $J'=24$, d) level, and (d) the ($v'=9$, $J'=61$, d) level of the ${}^7\text{Li}_2 B {}^1\Pi_u-X {}^1\Sigma_g^+$ spectrum in the presence of argon at a pressure of 5 torr.

ments:

(1) They should be sufficiently intense (compare the strong intensity variation within one fluorescence series as illustrated in Table II and III of I).

(2) The polarization dependence of the grating spectrometer must be taken into account in order to compare the intensities of different satellites. Both the parent lines and their satellites are polarized; however, their degrees of polarization are usually quite different and can even have opposite signs.⁷ Therefore, the relative sensitivity of the spectrometer for light polarized in a horizontal and a vertical plane was measured as a function of wavelength. In our case the spectrometer was polarization independent within $\pm 3\%$ between 5200 and 5300 Å. It was therefore preferable to use fluorescence lines in this region. Where this was not possible, the degree of polarization of both the parent and the satellite lines was measured and a correction (on the order of a few percent) was applied to the relative satellite intensity.

(3) It is essential to select fluorescence lines which are sufficiently far removed from any other strong lines. The satellite intensities can be seriously distorted by interference from overlapping "foreign" lines—either fluorescence lines from a different series (which is

excited simultaneously with the series under study) or their satellites. This is particularly important in the case of ${}^6\text{Li}{}^7\text{Li}$ fluorescence, excited by 4765 Å, since this laser line simultaneously excites three other series in ${}^7\text{Li}_2$ and ${}^6\text{Li}_2$. Even with no "foreign" interference, the satellites of one and the same fluorescence line may overlap each other, particularly those belonging to ΔJ jumps by several units. The spectral resolution, therefore, has to be rather high (varying from 0.2 Å FWHM for ${}^6\text{Li}{}^7\text{Li}$ to 1.4 Å for the weak Q series excited by the 5145-Å laser line). Even then, it is important to select a favorable parent line, since the pattern of satellite positions is not exactly the same around different parent lines.

All observed satellites were identified by comparing their wavelengths, as obtained from the recorder chart, with wavelengths calculated using the improved Li_2 molecular constants from I. The intensity of each satellite was expressed as a percentage of the parent fluorescence line, where corrections were made for the usually small drift in the parent line intensity during a measurement.

In a few cases satellites around several fluorescence lines belonging to the same series were studied. Their intensities relative to the parent line intensity, at a

TABLE I. Fluorescence lines whose collision-induced satellites have been studied.

Molecular species	λ_{ex} (Å)	λ_n (Å)	v'	J'	Δ -doublet component	Illustration of pressure dependence
$^7\text{Li}_2$	4765	4931.5	4	24	d	Figure 3(d)
$^7\text{Li}_2$	4765	5250.1	4	24	d	
$^6\text{Li}^7\text{Li}$	4765	$\left\{ \begin{array}{l} 4927.0 \\ 4933.4 \end{array} \right.$	5	9	c	
$^6\text{Li}^7\text{Li}$	4965	5051.2	0	45	d	Figure 3(f)
$^6\text{Li}^7\text{Li}$	4965	5138.8	0	45	d	
$^6\text{Li}^7\text{Li}$	4965	5227.7	0	45	d	
$^7\text{Li}_2$	4880	$\left\{ \begin{array}{l} 4800.2 \\ 4819.1 \end{array} \right.$	2	31	c	
$^7\text{Li}_2$	4880	$\left\{ \begin{array}{l} 4960.7 \\ 4980.5 \end{array} \right.$	2	31	c	
$^7\text{Li}_2$	4880	$\left\{ \begin{array}{l} 5211.7 \\ 5232.7 \end{array} \right.$	2	31	c	
$^7\text{Li}_2$	4880	$\left\{ \begin{array}{l} 5298.1 \\ 5319.6 \end{array} \right.$	2	31	c	Figure 3(b)
$^7\text{Li}_2$	5145	$\left\{ \begin{array}{l} 4743.4 \\ 4761.3 \end{array} \right.$	3	30	c	Figure 3(a)
$^7\text{Li}_2$	5145	$\left\{ \begin{array}{l} 5691.7 \\ 5717.1 \end{array} \right.$	9	38	c	Figure 3(c)
$^7\text{Li}_2$	5145	5747.0	7	61	d	Figure 3(e)

given pressure, were the same within 10% for different parent lines, provided the resolution was sufficient. In the worst case, however, the relative satellite intensities in the high pressure region disagreed by as much as 50% although the main trends in the satellite intensity pattern were still independent of the particular parent line chosen. Table I lists the fluorescence lines whose collision-induced satellites were studied.

RESULTS

Typical examples of satellite lines induced by collisions are presented in Figs. 1 and 2. The main feature of these patterns is that they show six prominent satellites. As already discussed in I, these six lines result from collisional transfer of energy in which the rotational

quantum number of the molecular level changes by $\Delta J = \pm 1$ or $\Delta J = \pm 2$.

In addition to the standard spectroscopic designation of each line by $P(J'')$, $R(J'')$, and $Q(J'')$, the P and R lines in Fig. 1 are also labeled according to their common J' level from which they originate (for Q lines, of course, $J' = J''$). This notation is more appropriate in our case since the ΔJ jump occurs between the J' levels.

The selection rule $s \leftrightarrow s$ and $a \leftrightarrow a$ governs⁸ the collisional transitions in $^7\text{Li}_2$. If the laser excites a P or an R line as in Fig. 1(a) and (b), then jumps by $\Delta J = \pm 1$ (and any other odd ΔJ) produce Q lines only, and jumps by $\Delta J = \pm 2$ (and any other even ΔJ) produce P , R doublets only. The reverse is true if the laser excites a Q line, as in Fig. 1(c) and (d). Since the symmetric

levels have even parity and the antisymmetric levels odd parity, the collisional transitions between rotational levels of the ${}^7\text{Li}_2 B {}^1\Pi_u$ state at the same time conserve parity.

In ${}^6\text{Li}{}^7\text{Li}$, which is a heteronuclear diatomic,⁹ the selection rule $s \leftrightarrow s$ and $a \leftrightarrow a$ is no longer meaningful, and any ΔJ jump produces both Q lines and P, R doublets. Consequently, Fig. 2 shows about twice as many prominent satellites as Fig. 1. However the ${}^6\text{Li}{}^7\text{Li}$ molecule represents only a small departure from the homonuclear case; it is apparent in Fig. 2 that the jumps by $\Delta J = \pm 1$ and $\Delta J = \pm 2$ that conserve parity are the most probable and the six corresponding satellites appear as the most intense.

An examination of the spectra in Fig. 1, particularly in (a) and (b), shows that jumps by $\Delta J = \pm 2$ are less probable than jumps by $\Delta J = \pm 1$. This is as expected and is in accordance with the observation on other molecules.¹⁻⁵ In Figs. 1(c) and 1(d) this rule is equally true, although less conspicuous from a first glance at the figures. However, it must be borne in mind that the intensities of a P and an R line originating from the same (v', J') level have to be summed in order to give a true measure of the population of that level by collisions.

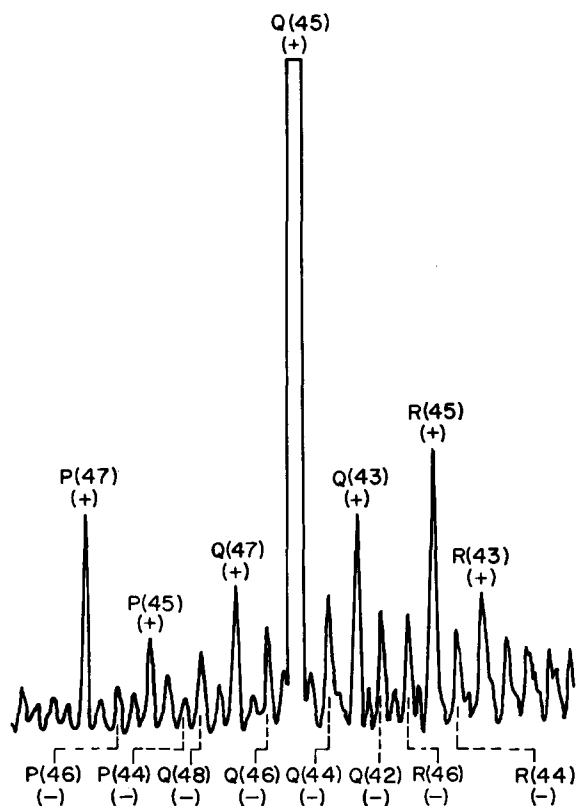


FIG. 2. Collision-induced satellite pattern accompanying the fluorescence at $\lambda = 5051.2 \text{ \AA}$ resulting from the excitation of the $(v' = 0, J' = 45, d)$ level of the ${}^6\text{Li}{}^7\text{Li } B {}^1\Pi_u - X {}^1\Sigma_g^+$ spectrum in the presence of argon at a pressure of 5 torr.

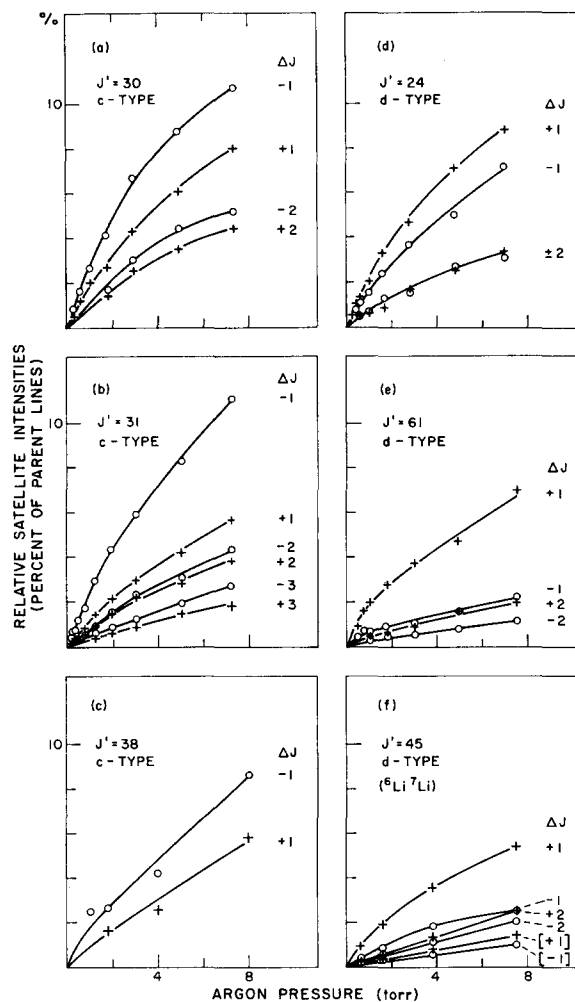


FIG. 3. Relative satellite line intensities as a function of argon pressure. The panels on the left, (a), (b), and (c), are for collisions with c -type Λ components of the upper state and the panels on the right, (d), (e), and (f) are for d -type Λ components.

This explains why in Figs. 1(c) and 1(d) the individual P and R lines arising from $\Delta J = \pm 1$ jumps appear to be as strong as the Q lines arising from $\Delta J = \pm 2$ jumps.

If we compare jumps of $\Delta J = +1$ to those of $\Delta J = -1$, another even more striking difference becomes apparent. In Figs. 1(a) and 1(b) jumps by $\Delta J = -1$ are favored over those by $\Delta J = +1$, while in Figs. 1(c) and 1(d) the reverse is true. On the other hand, all jumps by $\Delta J = +2$ and -2 shown in Fig. 1 are of about the same intensity.

In Fig. 2 the same propensity is illustrated for satellites around a parent Q line in ${}^6\text{Li}{}^7\text{Li}$. The $P(47)$ and $R(45)$ lines that result from the $\Delta J = +1$ jump are much more intense than the $P(45)$ and $R(43)$ lines that result from the $\Delta J = -1$ jump. The intensities of the $Q(47)$ and $Q(43)$ lines that result from the $\Delta J = \pm 2$ jumps, respectively, are again more similar to each other.

In order to verify that the satellite lines are mostly

the consequence of single collision events (as has been implicitly assumed so far) the pressure dependence of the relative satellite intensities was studied. Figure 3 illustrates the results from which it is obvious that in the low pressure region a linear relationship exists between the satellite intensities and the pressure. This confirms the above assumption. In this pressure regime the average time between collisions is longer than the radiative lifetime,¹⁰ so that a molecule usually suffers no more than one rotational inelastic collision before it radiates. From the rate of growth of the relative satellite intensities with pressure, the various absolute cross sections for rotational transfer can be deduced provided the radiative lifetime and the quenching cross section of the parent level are known.

The curvature of the plots at high-pressure (Fig. 3) results from the effect of secondary collisions. In addition to radiative depopulation of the collisionally populated levels, we must include secondary collisional depopulation, which introduces a pressure-dependent term (or sum of terms) in the loss rate.

Figure 3 gives twofold evidence that the $\Delta J = \pm 2$ jumps are also single collision events. First, the pressure plots pertaining to these satellite lines are again linear. Second, the $\Delta J = \pm 2$ satellites relative to the $\Delta J = \pm 1$ satellites are much more intense (about 50% of the latter) than the $\Delta J = \pm 1$ satellites are relative to the parent lines (about 10% at the highest pressures). If the $\Delta J = \pm 2$ jumps were the result of two successive jumps by one unit of J each, they then should have about the same intensity relative to the $\Delta J = \pm 1$ satellites as the latter have relative to the parent lines.

Figure 3 also illustrates the propensity rules for $\Delta J = \pm 1$ jumps and $\Delta J = \pm 2$ jumps that we discussed with reference to Figs. 1 and 2. Note that these propensities are maintained over the pressure range we investigated.

In Fig. 3(b) the pressure dependence of satellite lines arising from $\Delta J = \pm 3$ jumps has been included. The $J' = 31$ fluorescence series was a particularly favorable case for reasons of intensity and resolution. It is evident from Fig. 3(b) that the propensity for the $\Delta J = \pm 3$ jumps is about as clearly pronounced as for the $\Delta J = \pm 1$ jumps and is in the same direction. Note that the propensity for negative over positive ΔJ changes is nearly absent in the $\Delta J = \pm 2$ jumps. Thus the propensity variation with $|\Delta J|$ does not parallel the transition probability variation which is seen to fall off monotonically with increasing $|\Delta J|$.

In Fig. 3(f) we present pressure plots of the $\Delta J = \pm 1$ jumps in ${}^6\text{Li}{}^7\text{Li}$ that change parity. From the linear dependence on pressure of these jumps, denoted by *brackets*, we conclude that these rotational transfers are also the result of single collision events. It is difficult to deduce what propensity might exist for the lines because of the possibility that they are blended by neighboring satellites. In fact Fig. 2, which refers to the $Q(45)$ line

at 5051 Å, shows that $Q(44)$ is slightly more intense than $Q(46)$, while Fig. 3(f), referring to the $Q(45)$ line at 5138.8 Å, shows the reverse. We feel it is likely that the $[\pm 1]$ jump occur with about the same probability, and thus resemble the $\Delta J = \pm 2$ behavior rather than the $\Delta J = \pm 1$ behavior. Figure 3(f) does not include the pressure dependence of the weak lines $P(46)$ and $R(44)$ in Fig. 2. However, these lines are particularly interesting since they represent transitions within the same rotational level, i.e., $\Delta J = [0]$, from the lower to the upper component of the Λ doublet. This energy difference is less than one wavenumber. The strong $P(47)$ and $R(45)$ lines in Fig. 2 demonstrate that the ${}^6\text{Li}{}^7\text{Li}$ molecule prefers to make transitions to much more distant levels that are of the same parity.

DISCUSSION

The earliest investigations of atomic and molecular spectra were characterized by the discovery of so-called *selection rules* that enabled us to predict which spectral lines would occur and which would be absent. These selection rules are based on the symmetries of the initial and final states combined with the knowledge of the electric or magnetic multipole character of the transition. As opposed to the transition of a molecule from one state to another by the emission of radiation, there is the possibility of transfer between states caused by collisions. Here the interaction seldom has a well-defined multipole character and, in addition, the transition probability for an individual collision depends on such parameters as the relative velocity, the impact parameter, the initial orientation, etc. A spectrum emitted by molecules in the presence of a foreign gas reflects the averaging over all possible binary collisions. Therefore, the collisional transfer will, in general, not be governed by rules having the same rigor as those governing radiative transitions. Nevertheless, the symmetries of the initial and final states of the molecule may be expected to influence the probability of any particular collision outcome. This will cause the molecule to have a propensity or predilection for collisional transfer into one state in preference to another. The discovery of such so-called *propensity rules*, which has been the object of our investigations, constitutes a first step in understanding the detailed nature of the collision process.

For collisions of the ${}^7\text{Li}_2$ and ${}^6\text{Li}{}^7\text{Li}$ $B\ ^1\Pi_u$ excited state with argon atoms, Figs. 1-3 show that in some cases $\Delta J = +1$ jumps are preferred over $\Delta J = -1$ jumps and in other cases vice versa, whereas $\Delta J = \pm 2$ jumps seem to be nearly equiprobable. These findings are observed for both even and odd values of J , and hence cannot be attributed to the over-all parity of the molecular state. Since these propensities are also true of ${}^6\text{Li}{}^7\text{Li}$ as well as ${}^7\text{Li}_2$, the s, a reflection symmetry can also be ruled out. Instead we are led to conclude that the rotational transfer probabilities for the two Λ

doublet components must be responsible for these observed propensities. All our trends illustrated in Figs. 1-3 support the empirical rule that jumps by $\pm\Delta J$ that do not alter the character of the Λ component are about equally probable but $\pm\Delta J$ jumps that are between one Λ component and another are such that $+\Delta J$ is more probable than $-\Delta J$ for $d \rightarrow c$ transitions while $-\Delta J$ is more probable than $+\Delta J$ for $c \rightarrow d$ transitions.

In order to seek an explanation for these propensity rules we must examine what distinguishes one Λ component from the other. We shall outline here the origin of Λ -type doubling¹¹ with particular emphasis on viewing this phenomenon in terms of simple physical models. Since the force field of a diatomic molecule possesses cylindrical symmetry about its internuclear axis, the orbital angular momentum of the electron cloud is quantized by its projection upon this axis in units of $\Lambda\hbar$. In the case that $\Lambda \neq 0$, the wavefunction for the electron cloud may be resolved into $\sin\Lambda\phi$ and $\cos\Lambda\phi$, where ϕ is the azimuthal angle about the internuclear axis. In the rotating molecule, the angle ϕ is measured from \mathbf{J} , and the valence part of the electronic charge distribution, proportional to $\sin^2\Lambda\phi$ and $\cos^2\Lambda\phi$, respectively, contributes differently to the moment of inertia of the molecule. This causes the energy levels for each J to be split into two components that can be described in terms of the energy levels of a slightly asymmetric top.¹¹ This splitting, which arises from the coupling between the electronic and rotational motions of the molecule, increases with J . For a nonrotating molecule all electronic states with $\Lambda \neq 0$ are doubly degenerate.

Let us specialize our discussion to a ${}^1\Pi$ electronic state ($\Lambda=1$). In Fig. 4 we present the charge density distributions for the two Λ components. Figure 4(a) corresponds to the upper Λ component designated by c , which has a $\cos^2\phi$ distribution and thus the smaller moment of inertia. Figure 4(b) corresponds to the lower Λ component designated by d , which has a $\sin^2\phi$ distribution and thus the larger moment of inertia. Note that although the energy separation between the Λ components is extremely small and often unresolved,¹² the shapes of the c -type and d -type charge distributions shown in Fig. 4 are strikingly different. This suggests that the propensity rules we have found are related to these differences in the charge density and encourages us to speculate further on the nature of the collision interaction mechanism.

In what follows we will restrict ourselves to a purely classical model although the full explanation of these propensities will no doubt involve semiclassical or quantum mechanical considerations.¹³ Since we will concentrate our attention on ΔJ jumps with energy changes much less than kT , no reference will be made to the Maxwell-Boltzmann velocity distributions of the colliding partners. Let $V_{c \text{ or } d}(\mathbf{r}, \theta, \phi; v, J)$ be the inter-

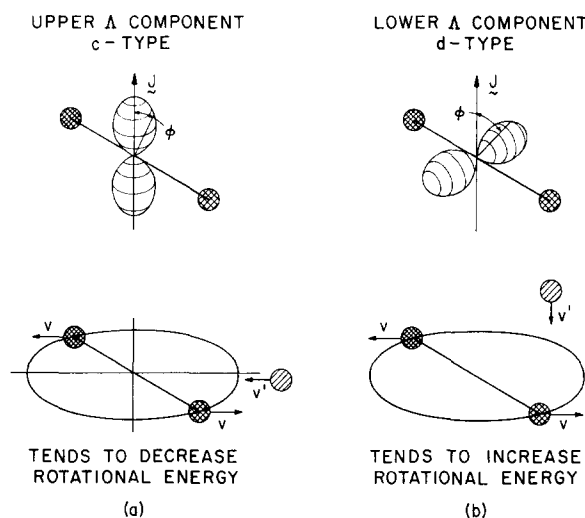


FIG. 4. Charge distribution of the π electron in the $\text{Li}_2 B {}^1\Pi_u$ electronic state for (a) the c -type and (b) the d -type component of the two Λ doublets. The lower half of (a) and (b) illustrates sample preferred collision trajectories that tend to cause $c \rightarrow d$ and $d \rightarrow c$ transitions, respectively.

action potential between an argon atom and an excited Li_2 molecule in the (v, J) state with c - or d -type Λ character, respectively. The arguments $(\mathbf{r}, \theta, \phi)$ specify the distance and orientation of the argon atom with respect to the center of mass of the Li_2 molecule.

When an argon atom and an excited Li_2 molecule approach each other, the colliding particles experience a force given by the gradient of the interaction potential, ∇V , and a torque given by $\mathbf{r} \times \nabla V$. The force, and hence the trajectory, is determined primarily by the angle-independent part of the interaction potential. On the other hand, the torque depends instead on the angle-dependent part of the interaction potential. The probability for rotational transfer can be calculated by solving the coupled equations of motion of this three-body system and determining the change in the magnitude of \mathbf{J} caused by the action of the torque integrated along the collision trajectory. Of course, a suitable average must then be taken over all possible collision trajectories.¹⁴

It might be supposed that almost all the torque is exerted over a small range around the distance of closest approach (the classical turning point) where the two collision partners spend the largest fraction of their time together. If this were true, the rotational transfer probability could be calculated assuming that the relative orientation of the molecule was fixed at one value throughout the entire collision.¹⁵ However, detailed classical calculations have shown that this approximation is not generally valid, and that in thermal collisions it is necessary to take into account the rotation of the molecule during the effective time of collision.¹⁴ In any

case, the classical calculations we have outlined above cannot be performed for the $\text{Ar}+\text{Li}_2^*$ system since the intermolecular potential is at present unknown.

The above discussion nevertheless provides a useful framework to judge qualitatively how a trial intermolecular potential would affect the rotational transfer process. Let us consider those collisions that alter the character of the Λ components. It seems reasonable to suppose that the collision trajectories most effective in causing the transition $c \rightarrow d$ or $d \rightarrow c$ would be those having components of motion parallel to the plane separating the two lobes of the charge distributions shown in Fig. 4 (so that one lobe is on one side of the plane and the other on the opposite side). For $c \rightarrow d$ transitions, Fig. 4(a) illustrates a collision of an argon atom with a velocity component parallel to the plane of rotation of the molecule. In the lower portion of Fig. 4(a) we picture the vectorial addition of this velocity with the rotational velocity of the two Li atoms. Since the magnitudes of the Ar and the Li velocities are comparable, collisions will occur predominantly between the Ar atom and the Li atom moving towards it. As a result, the rotational velocity of the Li_2 molecule will predominantly be reduced. This causes $-\Delta J$ jumps to be more probable than $+\Delta J$ jumps, in accord with the propensity rule we have found. For $d \rightarrow c$ transitions, Fig. 4(b) shows that the velocity of the argon atom always has a component perpendicular to the plane of rotation of the molecule. If the velocity of the argon atom and either one of the Li atoms is vectorially added, as is illustrated in the lower portion of Fig. 4(b), the resultant velocity is larger than the initial rotational velocity of the Li_2 molecule, thus causing $+\Delta J$ to be more probable than $-\Delta J$ jumps, again in accord with the propensity rule. For collisions that preserve the character of the Λ component, such as jumps by $\Delta J = [\pm 1]$ or $\Delta J = \pm 2$, the orientation of the charge distributions shown in Fig. 4 evidently plays little role. The ± 1 or $\Delta J = \pm 2$, the orientation of the charge distributions shown in Fig. 4 evidently plays little role. The molecule then behaves as a rigid rotor, which has been previously observed¹⁻⁵ to have little preference for jumps by $\pm \Delta J$.

We expect that the propensity rules for various rotational transfers that we have found here, will be generally applicable to other Π electronic states.¹⁶ For example, it is intriguing to speculate what role these propensity rules might play in causing the population inversion found in the ${}^2\Pi$ ground state of the interstellar OH radical that is responsible for its intense radio emission.¹⁷ For Δ states and higher states of $\Lambda \neq 0$, the charge distribution patterns ($\sin^2 \Delta\phi$ and $\cos^2 \Delta\phi$) are of a rosette form and the propensities we have found for rotational transfer may be reduced. Analogous propensities in the rotational transfer of polyatomic molecules possessing l -type doubling¹⁸ may also exist.¹⁹ In conclusion, much more effort is required, both

experimental and theoretical, to discover the validity and scope of propensity rules in rotational transfer.

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⁶ R. Velasco, Ch. Ottinger, and R. N. Zare, *J. Chem. Phys.* **51**, 5522 (1969).

⁷ A classical explanation for this phenomena is as follows: The collision causes J to change without altering appreciably the M state distribution. The radiation is thus of the type ($P \uparrow$, $Q \downarrow$), ($Q \uparrow$, $P \downarrow$), ($R \uparrow$, $Q \downarrow$), or ($Q \uparrow$, $R \downarrow$) whose degree of polarization in the limit of large J is $P = -\frac{1}{3}$ [See R. N. Zare, *J. Chem. Phys.* **45**, 4510 (1966)]. Analogous polarization differences have been observed in Na_2 by W. Demtröder and M. McClintock (private communication).

⁸ See G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1950), pp. 130–140. For homonuclear diatomics having no nuclear spin the prohibition of intercombinations between symmetric and antisymmetric levels is perfectly rigorous. For the ${}^7\text{Li}_2$ molecule composed of nuclei with spin three-halves this selection rule no longer holds absolutely since there is the possibility of collisions that simultaneously alter the rotational and nuclear-spin states. However, such $s \leftrightarrow a$ interconversions are extremely rare. See the work of G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.* **37**, 2907 (1962) on the measurement of the relaxation rate of equivalent F atoms in the gas phase.

⁹ If the two nuclei in a diatomic molecule have the same charge, as in ${}^7\text{Li}_2$ and in ${}^6\text{Li}{}^7\text{Li}$, the force field in which the electrons move has a center of symmetry. The electronic eigenfunctions are then classified by g or u depending on whether or not they remain unchanged or change sign under inversion through this center. See Ref. 8, pp. 217–218.

¹⁰ The radiative lifetime of the ${}^7\text{Li}_2 B {}^1\Pi_u$ state is presently unknown. However, if we assume its behavior is comparable to the $B {}^1\Pi_u$ state of Na_2 [See M. McClintock, W. Demtröder, and R. N. Zare, *J. Chem. Phys.* **51**, 5509 (1969)] or the $B {}^1\Pi_u$ state of K_2 [See W. J. Tango, J. K. Link, and R. N. Zare, *J. Chem. Phys.* **49**, 4264 (1968)], the molecular radiative lifetime will be less than the parent Li $2p$ atom, i.e., less than 25 ± 1 ns [See W. S. Bickel, I. Martinson, L. Lundin, R. Buchta, J. Bromander, and I. Bergström, *J. Opt. Soc. Am.* **59**, 830 (1969)].

¹¹ For a more complete treatment see R. de L. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, Cambridge, England, 1930); L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), Chap. XI.

¹² C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Co., New York, 1955).

¹³ For a review of theoretical studies of rotational transfer in molecular collisions see K. Takayanagi in *Advances in Atomic and Molecular Physics*, D. R. Bates and I. Estermann, Eds. (Academic Press Inc., New York, 1965).

¹⁴ Such calculations have been performed by R. J. Cross, Jr. and D. R. Herschbach, *J. Chem. Phys.* **43**, 3530 (1965).

¹⁵ E. A. Mason, J. T. Vanderslice, and J. M. Yos, *Phys. Fluids* **2**, 688 (1959); L. Monchik and E. A. Mason, *J. Chem. Phys.* **35**, 1676 (1961); **36**, 2746 (1962).

¹⁶ Of course if certain other features of the collision interaction are present, such as long range dipole-dipole forces, they may predominate over the propensities we have discussed.

¹⁷ See B. J. Robinson and R. X. McGee, *Ann. Rev. Astron. Astrophys.* **5**, 183 (1967).

¹⁸ For a discussion of *l*-type doubling, consult H. C. Allen, Jr. and P. C. Cross, *Molecular Vib-Rotors* (John Wiley & Sons, Inc.,

New York, 1963). See also T. Oka, *J. Chem. Phys.* **47**, 5410 (1967).

¹⁹ Considerable progress has been made in elucidating the rotational transfer propensities of ground-state polyatomics through the method of microwave double resonance, when it is applicable. See A. P. Cox, G. W. Flynn, and E. B. Wilson, Jr., *J. Chem. Phys.* **42**, 3094 (1965); T. Oka, *ibid.* **45**, 754 (1966); **47**, 13 (1967); **47**, 4852 (1967); **48**, 4919 (1968); **49**, 3135 (1968); **49**, 4234 (1968); A. M. Ronn and E. B. Wilson, Jr., *ibid.* **46**, 3262 (1967); R. G. Gordon, P. E. Larson, C. H. Thomas, and E. B. Wilson, Jr., *ibid.* **50**, 1388 (1969).

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Nitroxide Radical-Metal Chelate Interactions

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We have investigated the interaction of some nitroxide radicals with a series of transition-metal acetylacetonate complexes by monitoring the linewidth of peaks in the ESR spectra of the radicals as a function of chelate concentration. The effect of the chelates on the NMR spectra of some diamagnetic materials was also investigated. The linewidths are found to vary with the number of spins on the metal and the geometry of the complexes.

INTRODUCTION

The interaction of the odd electrons on transition metals with the protons on water molecules results in a reduction of the relaxation times of the protons.^{1,2} A similar reduction in proton relaxation times is found when organic radicals are added to various types of solvents.³ The electron-proton dipole-dipole interaction is generally the largest term in the equations for the proton relaxation times. In some cases it has also been necessary to include a second term which describes a scalar interaction. The dipolar term falls off rapidly with distance, and the largest interaction is between the electrons and protons on molecules in the metal's first solvation sphere. In cases in which bulk solvent and solvent in the first solvation sphere are rapidly exchanging, one observes a time average of the two magnetic environments.

The equation for the transverse relaxation time is

$$(1/T_2) = \left(\frac{4}{3\hbar^2}\right) S(S+1) P (g^2 \beta^2 \gamma_n^2 / r^6) \\ \times [7\tau_c + 13\tau_c(1 + \omega_s^2 \tau_c^2)^{-1}] \\ + \frac{1}{3} S(S+1) P (A^2 / \hbar^2) [\tau_e + \tau_e(1 + \omega_s^2 \tau_e^2)^{-1}], \quad (1)$$

with $(\tau_c)^{-1} = (\tau_e)^{-1} + (\tau_r)^{-1}$. In this expression P is the fraction of molecules' interacting with the metal, r is the effective separation between the electrons and the protons, τ_e is the correlation time for exchange coupling, τ_r is the rotational correlation time, ω_s is the electrons' Larmor frequency, and A is the electron-nuclei coupling constant. In cases in which the concentration of solvent

is much larger than that of the metal ions, P is given by

$$P = Mn/N_s, \quad (2)$$

where M is the metal concentration, n is the solvation number, and N_s is the solvent concentration.

We have investigated the interactions of a series of transition-metal acetylacetonate (AcAc) complexes

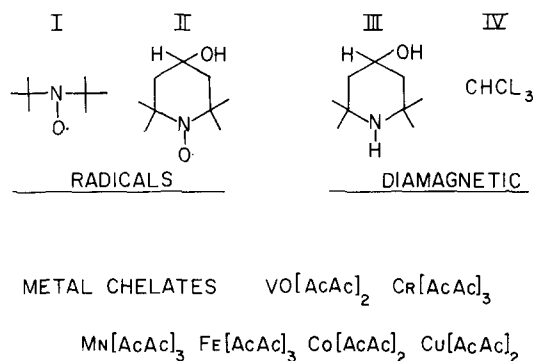


FIG. 1. Compounds investigated.

with two nitroxide radicals. The linewidths of the peaks in the ESR spectra of the nitroxide radicals were monitored as the concentrations of the metal chelates were varied. In these cases one is dealing with the dipole-dipole and exchange interactions of the electrons on the metals and the electrons on the radicals. If γ_n^2 is replaced by γ_e^2 one should be able to use Eq. (1) to describe the line broadening of the ESR spectra. The