Radiative Lifetime of the $B ^{1} \Pi_u$ State of $K_2$*

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Using the phase-shift method, a radiative lifetime study has been made of the $K_2 B ^{1} \Pi_u$ molecule excited by the 632.8-nm line of an He-Ne laser. The radiative lifetime extrapolated to zero pressure is found to be $\tau = 12.4 \pm 0.3$ usec, where the error represents three standard deviations of the statistical uncertainty. A simple valence-bond model for the molecular transition is proposed which predicts that the radiative lifetime of the $B ^{1} \Pi_u$ state of the dialkalis will be shorter, by about a factor of 2 or more, than the lifetime of the parent atomic $P$ state into which the excited alkali dimer separates. The results of these calculations are compared with the experimentally observed lifetimes for several vibrational states of Na$_2$ and K$_2$.

I. INTRODUCTION

An important parameter describing the electronic structure of atomic or molecular states is the electronic oscillator strength, or the closely related quantity, the radiative lifetime. Atomic oscillator strengths have been extensively studied, both experimentally and in theory, largely under the stimulus of astrophysics. On the other hand, although molecular lifetimes and oscillator strengths have been examined theoretically, mainly for the purpose of better understanding the nature of the electronic states of molecules, until recently very few measurements of the radiative lifetimes of molecules in the gas phase have been made.

The last few years have seen an increase in the number of molecules which have been studied for the purpose of determining electronic oscillator strengths. In this field lasers show a clear advantage over conventional light sources such as atomic resonance lamps since they allow one to prepare molecules in only one, or at the most, a very few vibronic states so that radiative lifetimes can be meaningfully determined as a function of vibrational quantum number. Lasers also provide the high intensities that are usually needed. Of course one is limited by the number of known laser transitions, but tunable dye lasers should make it possible to examine virtually any molecule that fluoresces in the visible or near-ultraviolet region of the spectrum. We report here the measurement of the radiative lifetime of the $B ^{1} \Pi_u$ state of $K_2$ determined by a laser phase fluorometer. This molecule is particularly convenient to study since resonance fluorescence is readily produced by the 632.8-nm transition of the He–Ne laser and its spectrum is rather well characterized. Although the interest in the lifetimes of the excited states of the alkali dimers such as $K_2$ is mainly theoretical, the techniques described here are generally applicable to other diatomic systems which have absorption features in the visible region of the spectrum.

The $A$ and $B$ states of the alkali dimers belong to a special class of molecular states (the “two-quantum” states of Kemble and Zener) that is characterized by strong transitions to the ground state even in the limit of large internuclear separation. The lifetimes of such states appear to be governed primarily by the nature of the corresponding atomic transitions, so long as the molecular interactions are relatively weak. This situation should be contrasted with “$V$–$V$” type transitions which occur between a valence ($V$) state and the ground ($V$) state of the molecule. Since both the ground and valence states arise from the same atomic configuration, the $V$–$V$ transitions are forbidden in the limit of infinite separation, and one would therefore expect that transitions of this kind would depend strongly on the detailed nature of the bonding in the molecule.

Most of the calculations of dipole strengths and transition probabilities for molecular systems have been made for valence transitions, since valence states are commonly the lowest-lying electronic states of molecules. For the reason just stated, these calculations are usually quite poor in predicting the oscillator strengths or lifetimes, even for simple systems such as $H_2$. In order to obtain reasonable agreement with the observed values one must include considerable configuration interaction.

Transitions of the sort encountered in the dialkali spectra, on the other hand, may prove to be more tractable. These molecules are characterized by small binding energies in the ground state, ranging from 1.03 eV for Li$_2$ to 0.45 eV for Cs$_2$, while also having rather large internuclear separations (in Li$_2$ for example, $r_c = 2.7 \times 10^{-8}$ cm for the ground state; for K$_2$, $r_c = 3.9 \times 10^{-8}$ cm). As a result they closely approach the chemists’ picture of purely covalent compounds, i.e., molecules that are held together solely by a sharing of the valence electrons with little or no distortion of the atomic shells. In such systems one expects that the transition moment will be essentially the atomic moment, modified slightly by exchange, etc. We will show that such a picture is indeed a valid way to regard these molecules and that a modified valence-bond theory accounts quite satisfactorily for the observed lifetimes. It must be emphasized at the outset,
however, that the alkali dimers are not typical, strongly bound diatomic molecules, and we are not justified in extending the theory to such systems.

II. EXPERIMENTAL

The principles of phase fluorometry are well known and have been described elsewhere. Briefly, resonance fluorescence is produced by means of sinusoidally modulated excitation. In the event that the decay of the excited state producing the fluorescence is exponential, the fluorescence will be modulated at the same frequency as the excitation, but will lag in phase. If the excitation frequency is $f$ (hertz), the phase shift is given by

$$\phi(f) = \arctan\left(2\pi f T\right),$$

where $T$ is the radiative lifetime of the excited state. If the power (averaged over many cycles of the optical frequency) of the exciting light in a bandwidth $df$ is $I_{ex}(f) df$, then the corresponding power $I_{fl}(f) df$ in the fluorescence is related to the excitation by

$$I_{fl}(f) df = I_{ex}(f) df / \left[1 + (2\pi f T)^2\right].$$

The phase fluorometer thus consists of a light source, modulator, and detector. Figure 1 shows the arrangement used in this experiment. The light was produced by an He–Ne laser that was modulated at a radio frequency by means of a Pockels cell consisting of a potassium dihydrogen phosphate (KDP) crystal and associated polarizing elements. With the optics shown in Fig. 1, the transmitted light reaching the K$_2$ cell had about 20% modulation at the fundamental $f$, with very little harmonic distortion. An attenuator placed in the optical path permitted us to vary the intensity of the excitation at the fluorescence cell without altering the phase of the modulation. The K$_2$ fluorescence cell, contained in a steel and firebrick oven, was fabricated of Corning 1720 glass to resist attack by the alkali; the temperature of the cell was measured by a thermocouple attached to it. The fluorescence was detected by a photomultiplier having an S-20 response. In order to reduce spurious modulation because of mechanical vibration in the KDP crystal, the entire apparatus was mounted on a steel surface plate.

A single-sideband phase detector, shown schematically in Fig. 2, was used to determine the phase of the fluorescent radiation. Such a detector effectively transfers the phase information of the radio-frequency carrier to a convenient audio frequency, in this case, 800 Hz. The phase of the 800-Hz signal can be readily determined by means of a precision phase shifter and phase-sensitive detector. Since the phase angle that is measured includes instrumental phase shifts, it is necessary to determine the phase of the modulated laser beam. This was done by replacing the fluorescence cell with a similar cell containing a colloidal suspension of gold in alcohol and measuring the phase of the scattered light. The chief advantage of the gold sol is that the Brownian motion of the particles renders the scattered light totally incoherent, eliminating any possible effects caused by coherent radiation falling onto the phototube. (The fluorescence is incoherent because it is spontaneous emission.)

In order to verify that systematic errors in the detector were minimal, a variable optical path was inserted into the system, providing a means of calibrat-
Fig. 2. The single-sideband phase detector. The output of the photomultiplier (PM) is heterodyned with a signal at a frequency $f - p$, where $p$ is 803 Hz. A tuned filter removes the sum frequencies, and the phase of the resultant 800-Hz carrier is determined by a precision phase shifter and a phase-sensitive amplifier (JB-5). The output of the amplifier is a null when the two inputs are in quadrature, as shown.

The phase shift (in degrees) caused by an optical path change of $L$ (meters) is

$$\phi(L) = 1.2003 f L,$$

if $f$ is expressed in megahertz. The result of measurements at 10.00 and 13.00 MHz for path lengths from 0–3.5 m gave a slope of $1.208 \pm 0.040 \text{ MHz}^{-1} \cdot \text{m}^{-1}$, indicating that there were no significant systematic effects in the phase detector. (Throughout this paper the indicated limits of error represent statistical confidence limits of 95%, i.e., three standard deviations.)

Because of the limited dynamic range of the detector, it was necessary to ensure that the signal amplitude was within the linear range of the amplifiers and mixer. To further reduce any errors from this source, the intensity of the scattered light from the reference cell was always adjusted to equal the fluorescent intensity and the phase shift of the reference was checked for each data point taken.

Although there is no a priori reason for assuming that the decay of $K_2$ should be nonexponential, there are nevertheless several effects which might prevent the direct application of Eq. (1) to the observed phase shift. These systematic errors may be conveniently classified as intensity, wavelength, or temperature dependent.

Because of the high power densities that are encountered in lasers, it is possible that saturation, pumping, or stimulated emission may occur in the fluorescing vapor, causing the apparent lifetime to change. Although stimulated emission is unlikely, pumping has been observed in the alkali dimers at power densities similar to the levels used in this experiment, and this could conceivably alter the phase shift. Analysis shows, however, that to first order pumping should not affect the phase shift of the fundamental; its principal effect is to alter the second harmonic in the fluorescence. It was, in fact, verified that the phase shift was independent of the incident power over a range 0.5–50 mW.

There are two wavelength-dependent effects that are significant. The first is due to the fact that the phase shift in the photomultiplier tube may not be independent of the (optical) frequency of the incident light because of the photovoltaic effect. Since the fluorescence is redder than the excitation, one might expect the fluorescence to have a larger apparent phase shift than that given by Eq. (1). If this effect is present, however, it should show a dependence on the voltage applied to the photomultiplier; no such effect was observed, and we conclude that it was absent. A second wavelength-dependent effect is the variation of the lifetime with vibrational level. The 632.8-nm excitation excites several $v'$ levels, principally $v' = 7$ and 8; each of these transitions of course arises from a different $v''$ level of the ground state. Since the Boltzmann distribution of the ground state is altered as the temperature is varied, one might expect the intensity distribution in the fluorescence to vary also, and, if $\tau$ depends significantly on $v'$, the lifetime should change also. As we will show in the next section, this dependence on vibrational quantum number is quite small, and may be neglected in this experiment.

There are four possible errors which depend on the temperature (or density) of the $K_2$ vapor. As the density is raised, one frequently encounters problems due to radiation trapping, leading to apparently longer lifetimes. However, the fact that most of the fluorescence was produced at wavelengths different from the pumping light, and most of the excited molecules returned not to the ground state but to some vibra-
tionally excited level of the ground state, suggests that this should not be a problem in this experiment.

If the detector responds to light scattered off the cell walls (so-called "wall scatter"), the observed phase will lie somewhere between the true phase lag of the fluorescence and the phase of the incident light, since the light reflected off the walls is scattered instantaneously. Since the scattered light is independent of the temperature while the fluorescence of course increases, the presence of scattered light manifests itself as a temperature-dependent phase shift. The effect is largest at low vapor densities. To reduce this problem, a filter (Corning CS2-64) was used that has an attenuation of $10^{6}$ for light at 632.8 nm. This filter reduces the fluorescence by only a factor of 10, so a rejection of $10^{5}$ for wall-scattered light is obtained. Even with this, at temperatures below about 200°C the effect of wall scatter is appreciable so the measurements reported here were all made above this temperature.

Since atomic resonance radiation is observed when the $K_2$ fluorescence is excited, it has been proposed that the reaction

\[ K_2^* + K \rightarrow K_2 + K^* \]  

(4)

is probably the dominant mechanism for quenching of the $K_2$ fluorescence.\textsuperscript{4} If this is so, the observed lifetime will appear to depend on the temperature. Assuming that the potassium vapor behaves as an ideal gas and the cross section $\sigma$ for Reaction (4) is independent of the temperature, the apparent radiative lifetime is given by

\[ \tau^{-1}(T) = \tau_0^{-1} + \Theta T^{1/2} \rho_K(T), \]  

(5)

where $\tau_0$ is the radiative lifetime at zero pressure, $\rho_K(T)$ is the density of the potassium atoms at temperature $T$, and $\Theta$ is a constant related to the cross section by

\[ \Theta = (12R/M_K)^{1/2}\sigma; \]  

(6)

where $M_K$ is the atomic weight of potassium and $R$ is the gas constant. Using the thermodynamic constants of Stull and Sinke\textsuperscript{15} the atomic density can be estimated from the temperature of the cell, since the vapor is in thermodynamic equilibrium with the liquid. Figure 3 shows the results of fitting the data obtained for $K_2$ to an equation of the form of (5). The data taken with the 0.5-mW laser are denoted by $O$, the 5-mW laser by $\bullet$, and the points shown as $\square$ were measured with the 50-mW laser. The line represents a linear least-squares fit to the data, with parameters given by Eqs. (7) and (8).

There is one other wavelength-dependent systematic effect which could affect the accuracy of the extrapolated value of the lifetime. Since atomic emission is present, if the detector responded to it, one might expect that the observed lifetime would lie somewhere between the atomic and molecular lifetimes. It should be pointed out, however, that the potassium vapor is optically thick at the temperatures used in this experiment and the atomic emission is severely trapped. As a result, the effective atomic lifetime is very long, and by Eq. (2), its contribution to the modulated fluorescence is negligible.

The depth of modulation is approximately given by $[\tau_K + (2\pi f)^2]^{-1}$ where $\tau_K$ is the lifetime of the trapped $K^*$ photons.

![Fig. 3. The experimental data for $K_2$. The measured rate $\Gamma$ is plotted against $T^{1/2}\rho_K(T)$ according to Eq. (5). The data taken with the 0.5-mW laser are denoted by $O$, the 5-mW laser by $\bullet$, and the points shown as $\square$ were measured with the 50-mW laser. The line represents a linear least-squares fit to the data, with parameters given by Eqs. (7) and (8). The intercept, determined by a linear least-squares fit to the data, is $8.040 \pm 0.074 \times 10^{-17}$ sec$^{-1}$, and the slope is $4.22 \pm 0.33 \times 10^{-11}$ sec$^{-1/2}$ cm$^3$. Some data points near the intercept have been omitted for clarity.]

III. THEORY

A. The Molecular Wavefunctions

For the reasons outlined in the Introduction, there is reason to believe that the atoms in the alkali dimers are only weakly interacting and that therefore a valence-bond picture should give an adequate representation of their electronic structure. The valence-bond wavefunctions for the ground and first excited states of the lighter alkali dimers can be written as

\[ |^{1}\Sigma_g^+\rangle = N_s[ s_a(1) s_b(2) + s_b(1) s_a(2) ] \]  

(9)

and

\[ |^{1}\Sigma_u^+\rangle = N_s[ s_a(1) p_{b\uparrow}(2) + s_b(1) p_{a\uparrow}(2) + p_{b\uparrow}(1) s_a(2) + p_{a\uparrow}(1) s_b(2) ] \]  

(10)
where the subscripts on the \( p \) orbitals denote the projection of \( p \) on the internuclear axis, which may be 0, +1, or -1. The normalization factors \( N_X \) and \( N_A \) can be expressed in terms of overlap integrals,

\[
N_X = (2 + 2S[000])^{-1/2}
\]

(11)

and

\[
N_A = (4 + 4S[000]S[110] + 4S[010])^{-1/2};
\]

(12)

the overlap integrals are defined to be the matrix elements

\[
S[LDm] = \langle Ana, m | Bnblbm \rangle
\]

(13)

between the atomic orbitals \( | Ana, m \rangle \) and \( | Bnblbm \rangle \) positioned on centers \( A \) and \( B \), respectively. For the moment, the nature of the atomic orbitals will be unspecified.

A certain difficulty arises when the \( \Pi_u \) state is considered, caused by the \( A \)-type doubling. The state actually consists of two nearly degenerate levels which can be labeled \( \Pi_u^+ \) and \( \Pi_u^- \), where the \( \pm \) sign denotes the Kronig reflection symmetry or parity of the electronic wavefunction. Since the dipole strength does not depend on which \( A \)-type component is excited, we may choose any convenient linear combination of the properly symmetrized orbitals having the proper parity to compute the lifetime. We use the function

\[
| \Pi_u \rangle = N_B \left[ s_a(1) p_{1-b}(2) + s_b(1) p_{1+a}(2) + p_{1+a}(1)s_b(2) + p_{1-b}(1)s_a(2) \right],
\]

(14)

where the normalization constant is

\[
N_B = (4 + 4S[000]S[111])^{-1/2}.
\]

(15)

### B. The Atomic Orbitals

In many molecular calculations, Slater or Gaussian orbitals are used as the atomic basis set. These functions offer the advantages that matrix elements between such functions are relatively easy to evaluate and, especially for Slater orbitals, small basis sets can give quite good estimates of the orbital energy. Unlike theHamiltonian operator, the dipole-moment operator weights most heavily the wavefunction far away from the orbital center; as a result functions which work well in predicting the energy of a system may be rather poor for determining the transition moment.

In 1949 Bates and Damgaard\(^{17}\) suggested that Coulomb functions be used to approximate the orbitals of valence electrons in atoms and ions. This method correctly predicts the asymptotic behavior of such electrons, but cannot be used close to the center of charge. The atomic oscillator strengths calculated from these functions are usually fairly close to reliable experimental values, and as a result they are frequently employed to estimate atomic lifetimes.\(^2\) They are, however, more difficult to use than simple one-term orbitals.

The radial Coulomb wavefunctions for the \( S \) and \( P \) states of the alkali atoms can be represented by the asymptotic forms

\[
R_S(r) = r^{-1}N_S^{-1/2}[(2x)^{n*} - n^*(n^* - 1) (2x)^{n* - 1}] \exp(-x)
\]

(16a)

and

\[
R_P(r) = r^{-1}N_P^{-1/2}[(2x)^{n*} + (2 + n^* - n^*) (2x)^{n* - 1}] \exp(-x),
\]

(16b)

where \( x = r/n^* \). The effective quantum number \( n^* \) is found from the Rydberg formula for the energy needed to ionize the state and is not necessarily an integer. To avoid the computational difficulties caused by non-integral values of \( n^* \), we approximated the “exact” Coulomb wavefunctions by functions having \( n^* = 2 \). Table I shows the effect of this approximation; the table compares the observed atomic transition moments with computed moments, using Slater orbitals, the exact Coulomb wavefunctions, and Coulomb functions with \( n^* = 2 \). In the worst case, \( Li \), the approximation \( n^* = 2 \) leads to a transition moment which is too large by approximately 15%.

### C. The Transition Moments and Lifetimes for the Alkali Dimers

Figure 4 shows the results of a calculation for the reduced molecular transition moment using the modified Coulomb functions described above for the \( X \Sigma_u^+ - A \Sigma_u^+ \) and \( X \Sigma_u^+ - B \Pi_u \) transitions of the lighter alkalis \( Li, Na, \) and \( K \). The total transition probability for emission from a given excited vibrational-rotational

### Table I. Observed and calculated values of \( \langle P || R || S \rangle^2 \)

<table>
<thead>
<tr>
<th>( J' )</th>
<th>Experiment</th>
<th>Exact Coulomb</th>
<th>Approx. Coulomb</th>
<th>Slater</th>
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<tr>
<td>Li</td>
<td>17.9</td>
<td>16.50</td>
<td>27.00</td>
<td>54.64</td>
</tr>
<tr>
<td>Na (( \frac{1}{2} ))</td>
<td>18.9</td>
<td>18.02</td>
<td>27.00</td>
<td>110.26</td>
</tr>
<tr>
<td>(( \frac{3}{2} ))</td>
<td>18.8</td>
<td>18.08</td>
<td>110.25</td>
<td></td>
</tr>
<tr>
<td>K (( \frac{1}{2} ))</td>
<td>24.3</td>
<td>24.87</td>
<td>27.00</td>
<td>209.98</td>
</tr>
<tr>
<td>(( \frac{3}{2} ))</td>
<td>24.0</td>
<td>24.69</td>
<td>209.94</td>
<td></td>
</tr>
<tr>
<td>Rb (( \frac{1}{2} ))</td>
<td>26.5</td>
<td>26.48</td>
<td>27.00</td>
<td>317.09</td>
</tr>
<tr>
<td>(( \frac{3}{2} ))</td>
<td>26.0</td>
<td>26.34</td>
<td>316.35</td>
<td></td>
</tr>
<tr>
<td>Cs (( \frac{1}{2} ))</td>
<td>31.2</td>
<td>29.04</td>
<td>27.00</td>
<td>466.01</td>
</tr>
<tr>
<td>(( \frac{3}{2} ))</td>
<td>30.1</td>
<td>29.75</td>
<td>462.27</td>
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</table>

\(^{a}\) In atomic units.


\(^{c}\) The effective quantum numbers \( n^* \) are taken from H. G. Kuhn, Atomic Spectra (Academic, New York, 1965).
level ($v'$, $J'$) is approximately

$$A(v', J') = (4G'/(9) \sum_{\tau} k_{\tau}^v q_{\tau} \left| \langle \Pi || R || \Sigma \rangle \right|^2, \quad (17)$$

where $G'$ is a statistical factor\(^\text{19}\) equal to 1, $k_{\tau}$\(^3\) the mean cubed frequency of the ($v'$, $v$) band, $q_{\tau}$ the Franck-Condon factor for the transition, and $\langle \Pi || R || \Sigma \rangle$ the reduced molecular transition moment. The quantity $r_{\tau}$ is the $r$ centroid, which may be approximately regarded as the mean value of the internuclear separation during the transition. Since the frequencies and Franck-Condon factors and $r$ centroids for several of the lower-lying states of Li\(_2\), Na\(_2\), and K\(_2\) are well known,\(^\text{10,13,20-22}\) it was possible to compute the radiative lifetime

$$\tau(v') = A_v v^{-1},$$

and this is shown in Table II. The table is restricted to relatively low $v'$ levels because the Franck-Condon factors for the higher $v$ states of the excited electronic configuration are not accurately known. Since the transition moment is nearly independent of the vibrational level, the chief variation in the lifetime is caused by the change in the mean cubed frequency. As a result, the ratio of the molecular to atomic lifetime $\tau(M_2) / \tau(M)$ is very nearly equal to the ratio of the cube of the transition frequency in the atom to the mean cubed frequency of the corresponding molecular band system. Indeed, simple sum rule calculations would seem to indicate that most of the molecular absorption is accounted for by transitions to the $A \Sigma^+_2$ and $B \Pi_u$ electronic states arising from combining a ground-state alkali M with an excited atom M* in its lowest $P$ state.

### IV. DISCUSSION

The experimental value of the K\(_2\) lifetime reported in Sec. II is $12.4\pm0.3$ nsec. We recall that this value is in fact a weighted average of the lifetimes of the $v'$ states which are actually populated (principally the $v'=6, 7,$ and 8 levels). It can be seen from Table II, however, that $\tau$ is relatively independent of $v'$, and, to the $\pm0.3$-nsec accuracy of our experiment, it is not possible to distinguish $v'=6, 7,$ or 8. Taking the mean of these values, we predict a lifetime for the observed K\(_2\) fluorescence of 12.1 nsec, in excellent agreement with our experimental value.

Recently several lifetimes have been reported for various excited vibrational levels of the $\Pi_u$ state of Na\(_2\). Using molecular level-crossing spectroscopy, McClintock, Demtröder, and Zare\(^\text{23}\) have determined the lifetime of the $v'=10$ level to be $\tau = 6.4\pm0.4$ nsec. McClintock and Cartwright\(^\text{24}\) have similarly measured $\tau$

<table>
<thead>
<tr>
<th>$v'$</th>
<th>Li(_2)(A)</th>
<th>Li(_2)(B)</th>
<th>Na(_2)(A)</th>
<th>Na(_2)(B)</th>
<th>K(_2)(B)</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>9</td>
<td>32.55</td>
<td>7.77</td>
<td>27.30</td>
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<tr>
<td>1</td>
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<td>27.35</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
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<tr>
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<tr>
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<tr>
<td>6</td>
<td>34.25</td>
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<tr>
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<td>7.95</td>
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<td>35.38</td>
<td>8.74</td>
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<td>...</td>
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<tr>
<td>12</td>
<td>35.57</td>
<td>8.86</td>
<td>...</td>
<td>...</td>
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</tr>
<tr>
<td>13</td>
<td>35.74</td>
<td>9.00</td>
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</table>

* Computed using Eq. (17) for Coulomb wavefunctions with $n^* = 2$.

### Table III. Comparison of observed and calculated lifetimes for excited states of K\(_2\) and Na\(_2\).

<table>
<thead>
<tr>
<th>Dimer</th>
<th>$v'$</th>
<th>$\tau_{obs}$ (nsec)</th>
<th>$\tau_{calc}$ (nsec)</th>
<th>$\tau_{obs}/\tau_{calc}$×100</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_2)(I(_3))</td>
<td>6</td>
<td>6.2±0.4</td>
<td>7.4</td>
<td>84%</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>6.7±0.3</td>
<td>7.5</td>
<td>89</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.4±0.2</td>
<td>8.0</td>
<td>80</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>6.6±0.4</td>
<td>...</td>
<td>...</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>7.0±0.4</td>
<td>...</td>
<td>...</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>&gt;b</td>
<td>7.1±0.4</td>
<td>...</td>
<td>...</td>
<td>28</td>
</tr>
<tr>
<td>K(_2)(I(_3))</td>
<td>7c</td>
<td>12.4±0.3</td>
<td>12.1</td>
<td>103</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>7e</td>
<td>9.7±0.3</td>
<td>12.1</td>
<td>80</td>
<td>28</td>
</tr>
</tbody>
</table>

* Not computed.

* Excited by the Ar(II) laser transition at 457.93 nm.

* Average over several states (see text).

* This work.
for \( v' = 6 \) and \( v' = 13 \), finding values of 6.2±0.4 nsec and 6.6±0.4 nsec, respectively. Baumgartner, Demtröder, and Stock,\textsuperscript{28} using a phase fluorometer of somewhat different design than ours, have also measured the lifetimes of several excited dialkali states. Table III summarizes all the results to date for \( \text{Na}_2 \) and \( \text{K}_2 \).

Baumgartner \textit{et al.} have repeated our measurement of the \( \text{K}_2 \) lifetime, obtaining a value of 9.7 nsec, which differs substantially from our value. Additionally, in their work the dependence of the radiative rate on the vapor pressure was markedly different; \( \Gamma \) was observed to decrease with increasing density. We are unable to offer an explanation of this discrepancy. The qualitative conclusion that the molecular lifetime is much shorter than the atomic lifetime of 28 nsec nevertheless appears to be clearly established.

We note that in \( \text{Na}_2 \) the agreement is also qualitatively correct; moreover, the theory predicts the observed behavior of the lifetime with vibrational state. We conclude from these results that the simple valence-bond theory proposed here does describe the behavior of the alkali dimers quite well, and we are encouraged to believe that such a model may prove to be a useful tool in understanding some of the excited states of the dialkalis, especially the interalkali dimers, \( \text{NaK}, \text{NaRb}, \) etc., and the heavy species \( \text{Rb}_2 \) and \( \text{Cs}_2 \), about which little is presently known.

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Note added in proof: Since this paper was submitted, S. E. Johnson, K. Sakurai, and H. P. Broida\textsuperscript{28} have reported the excitation of four \( \left| v', J' \right\rangle \) levels of the \( \text{Na}_2 \) \( 1 \Sigma_{u}^+ \) state using the 6328 and 6401 Å lines of a helium–neon laser. Based on collisional relaxation studies they estimated the radiative lifetime to be \( \geq 1 \times 10^{-7} \text{ sec} \), in marked disagreement with our predictions shown in Table II, viz., 27–32 nsec. However, they have since made direct lifetime measurements\textsuperscript{27} and they have been able to place an upper bound on the radiative lifetime of \( 5 \times 10^{-8} \text{ sec} \).

\textsuperscript{*} This work is based on a thesis by W. J. Tango submitted to the University of Colorado in partial fulfillment of the requirements for the Ph.D. degree in Chemical Physics.

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\textsuperscript{5} E. C. Kemble and C. Zener, Phys. Rev. 33, 512 (1929).


\textsuperscript{8} S. Rothenberg and E. R. Davidson, J. Mol. Spectrosc. 22, 1 (1967).


\textsuperscript{11} F. W. Loomis and P. Kusch, Phys. Rev. 46, 292 (1934).


\textsuperscript{13} W. J. Tango, thesis, University of Colorado, 1969 (available from University Microfilms, Ann Arbor, Mich.). A more complete description of the phase fluorometer may be found in this reference as well as a discussion of the derivation of Eq. (1).


\textsuperscript{19} Because of the \( A \)-type doubling in the II state, there is a degeneracy associated with the electronic state, so that the total multiplicity of a given rotational state is \( 2(2J+1) \). However, since the two substates have different parity, it is possible to excite only one of them, in which case the apparent degeneracy is simply \( 2J+1 \). Reference 6 has termed this extra factor the electronic degeneracy or \( G \) factor. The factor of 9 in the denominator of Eq. (17) arises from the fact that we have employed the \textit{reduced} transition moment rather than the usual dipole transition moment (Mulliken's \( D \)). Although this usage is not common in molecular calculations, it conforms to the common practice in atomic physics. A more detailed discussion of this notation may be found in B. W. Shore and D. H. Menzel [\textit{Principles of Atomic Spectra} (Wiley, New York, 1968)].


\textsuperscript{22} W. R. Frederickson and C. R. Stannard, Phys. Rev. 44, 6321 (1933).


\textsuperscript{24} M. McClintock and D. Cartwright (private communication).

\textsuperscript{25} G. Baumgartner, W. Demtröder, and M. Stock, Z. Physik 232, 462 (1970). We thank Dr. Demtröder for making this information available to us prior to publication.


\textsuperscript{27} S. E. Johnson, K. Sakurai, and H. P. Broida (private communication).