HIGH POWER GAS LASERS BASED ON ALKALI-DIMER
A-X BAND RADIATION

by

George York and Alan Gallagher

NOTE: The material contained in this report will not be published in
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Abstract

The $A^1\Sigma^+_{u}$ state of the alkali dimer molecules is displaced to larger radii than the ground $X^1\Sigma^+_{g}$ state, yielding an emission band displaced toward longer wavelengths than the absorption band. Absorption at the emission wavelengths is also limited due to the small equilibrium fraction of atoms bound in the $X^1\Sigma^+_{g}$ state. The possibility of net gain in the emission band for a buffered alkali plasma is considered and found to be feasible if the $a^3\Pi_{u}$ state does not predissociate or quench rapidly due to buffer gas collisions. Electrical conversion efficiency in excess of 50% also appears feasible under these circumstances. The potential laser wavelengths for the various alkalis are in series of tunable bands between 0.7 and 1.2 μm. Stored energy densities in excess of 1 J/ℓ and total pulse energies of 1000 J/ℓ appear feasible at plasma electron densities of $10^{15}$/cm$^3$. The effect of alkali dimer absorption on possible alkali-noble gas excimer lasers is also considered.
I. INTRODUCTION

There is considerable current interest in the generation of high efficiency, high power density, short-pulse laser systems, particularly for use in laser-induced fusion. Such systems require: operation between levels whose separation is not very much smaller than the excitation energy of the upper state; efficient energy deposition into the upper laser level; and, an optical cross section that is not so large that superradiance occurs before the desired energy storage capacity is reached. It would also be advantageous to generate such a system which can operate in the visible or near visible and which can sustain a high excitation energy density. In this report we describe the optical properties of a medium that may satisfy the above requirements. The system considered is the A-X band of the alkali dimer molecules which has an inversion mechanism similar to that of dye lasers and the H₂ laser; the fluorescence is concentrated at longer wavelengths than the absorption. However, the proposed alkali system relies on atomic excitation followed by excimer formation (recombination into the A-state) as in the LiXe system proposed by Phelps. We also report the effects of the presence of dimer molecules, with their high absorption cross sections, on the operation of the proposed alkali-rare gas laser systems such as LiXe.

The proposed alkali dimer and alkali-rare gas systems, unlike the rare-gas dimers, operate in the 7000-12000 Å region, where mirrors, lenses and other optical components have low fundamental and harmonic losses. Further, the excimers can be formed by direct electrical excitation of the free alkali resonance transition (ns-np) followed by recombination. The typical cross section of ~50 Å² for this electron excitation greatly exceeds all other low-energy inelastic cross sections...
and offers a very efficient means of collecting the input energy into the laser upper level.

Both the buffered alkali dimer system proposed here and the alkali-rare gas system described in Ref. 2 operate at similar gas densities and plasma conditions. In fact both will be present simultaneously and must be considered regardless of which dominates the optical properties. The A-X band of the alkali dimers and alkali-rare gas molecules extend from the alkali resonance line far to the red. In both cases the ratio of stimulated emission to absorption coefficients increases rapidly with increasing wavelength, so that the optimum laser gain occurs near the longest wavelengths associated with each band, but where the emission band is still intense. With the exception of LiXe versus Li$_2$, the alkali-dimer A-X bands extend to longer wavelengths than the alkali-rare gas bands. Thus the alkali dimer absorption is quite serious in the region where one might otherwise obtain alkali-rare gas laser action, but the converse doesn't hold. The alkali-rare gas optical properties can be ignored in considering alkali-dimers for laser action, excepting again LiXe versus Li$_2$. For this reason we have included a section in this report on the influence of alkali-dimer absorption on possible alkali-rare gas lasers (Sec. IV).

At low rare-gas densities ($<10^{19}$/cm$^3$) the alkali-rare gas systems cannot operate whereas the alkali dimers may exhibit gain. This low density operation is considered in Sec. III; it appears to be much less efficient and does not allow high-power operation. The high-pressure system is the primary focus of this study since it might yield high-power operation; it is considered in Sec. II.

The feature of the alkali dimer A-X system that makes net gain at
some wavelengths feasible is displaced potentials; i.e., the minimum of the A state is at a larger radius than that of the ground X state. This is the well-known feature responsible for net gain in dye lasers and the $H_2$ molecular laser. Its effect on absorption and stimulated emission coefficients in high pressure systems can be characterized by the same techniques used by Phelps to describe Xe$_2$ and LiXe excimer lasers, and is as follows.

If the nuclear motions in the X and A states are in thermal equilibrium at the gas kinetic temperature (T) due to collisions with the buffer gas, then the nuclear populations at each radius are, in the classical limit, proportional to $\exp[-\beta X(R)]$ and $\exp[-\beta A(R)]$ respectively,$^4$ where $X(R)$ and $A(R)$ are the adiabatic potentials in the X and A states and $\beta = 1/kT$. (The vibrational and rotational relaxation of the A state must be faster than the radiative rate.) Thus, the thermalized populations are concentrated in the region of the potential minima ($R_{eX}$) and decrease exponentially with potential height above the minimum. Now, the classical Franck-Condon principle (CFCP) asserts that molecules will radiate or absorb photons of energy $\hbar \nu = \Delta V(R) = A(R) - X(R)$ when the nuclei are separated by $R$. Therefore, the thermal distribution function, combined with the CFCP, means that X-state molecules will absorb near the wavelength corresponding to the difference potential at the minimum of the X state ($R_{eX}$); i.e. $\lambda_{Abs} \approx \hbar c/\Delta V(R_{eX})$. Emission, however, will be concentrated at the wavelengths near $\hbar c/\Delta V(R_{eA})$. Since $\Delta V$ decreases rapidly from $R_{eX}$ to $R_{eA}$ (cf. Fig. 1b), this emission is red-shifted from the absorption band. Thus, to achieve net gain at these longer wavelengths it is only necessary, thanks to the exponential factors, to excite a small fraction of the molecules to the A-state. The small X-
state binding, which yields a large dissociation fraction in the ground state, helps toward achieving this net gain. Below we will show that the threshold for net gain is $\frac{\text{Na}_2(\text{A state})}{\text{Na}_2(\text{X state})} \approx 0.05$, or equivalently, $\frac{\text{Na}_2(\text{A state})}{\text{Na}} \approx 0.002$. Similar or smaller fractions apply in the $\text{K}_2$ case, and probably in the $\text{Rb}_2$ and $\text{Cs}_2$ cases as well, but not for $\text{Li}_2$. The feasibility of achieving such fractions depends on many plasma collision rates, which we discuss below.

In Sec. II we give a series of short, approximate calculations and arguments concerning the optical properties of the medium, the collisional mechanisms and efficiency for producing A-state molecules, energy deposition and storage, gas heating, electron and current density requirements, alkali and buffer gas density considerations, and timing issues. In addition we describe the optical properties of the A-X transition for all the alkali dimers as accurately as is possible with current knowledge of the potentials and dipole moments. The spectra are treated as continua using the classical arguments of Ref. 4. At high buffer gas densities the lines are blended and the continuum spectrum is appropriate, but at low densities they are resolved and the continuum approximation is no longer accurate. The gain per excited molecule is much greater in the low-pressure limit, and many other characteristics of the medium are changed. We discuss the low-pressure laser system in Sec. III.
II. HIGH PRESSURE PULSED LASER SYSTEM

A. Optical Properties of the Alkali Dimer A-X Band

An adiabatic-state energy diagram of the ground and first excited configurations of Li₂, which is typical of all of the alkalis, is given in Fig. 1a. Here the X, A and B states have been accurately determined experimentally,⁵ while little is known about most of the other states. The other excited states are drawn in accordance with the qualitative guidelines of Mulliken,⁶ while the repulsive ground state \((x^3\Sigma_u^+)^\) is that of a recent calculation by Kutzelnick et al.⁷ The A and X state potentials and the difference potential \(\Delta V = A(R) - X(R)\) are given with higher resolution in Fig. 1b. The four lowest states of Na₂ are given in Fig. 2a. Here the \(X^1\Sigma_g^+\) and \(A^1\Sigma_u^+\) states are from optical data⁸ and the \(x^3\Sigma_u^-\) and \(a^3\Pi_u^-\) states from a calculation by Bertocci and Wahl.⁹ High resolution A and X-state graphs for Na₂ are shown in Fig. 2b and for K₂ in Fig. 3. The corresponding graphs for Rb₂ and Cs₂ are not given due to lack of information. In the following discussion we use the Na₂ case as the example of most interest, and then give the results of applying equivalent arguments to the other alkali dimers.

The equilibrium constants, \(K_A\) and \(K_X\), of the A and X states \((K_A = [\text{Na}_2(A^1\Sigma)]/[\text{Na}][\text{Na}^*])\) can be calculated to a few percent accuracy from the potentials using⁴:

\[
K_i = \frac{g_i}{g_f} \int_{R_{\text{min}}}^{\infty} \, d^3\text{R} \, e^{-\beta V_i(\text{R})} \{P[3/2, -\beta V_i(\text{R})]\}
\]

(1)

where \(V_i(\infty) = 0\), \(g_i\) and \(g_f\) are the statistical weights of the \(i\)th adiabatic state and parent atomic state, respectively, \(P(3/2,m)\) is the normalized incomplete gamma function,¹⁴ which is approximately unity in
Fig. 1a. Overview of the lowest electronic states of Li₂. The other alkalis have similar structures. Data sources and accuracy are discussed in the text.
Fig. 1b. Expanded view of the $A^1\Sigma_u^+$ and $X^1\Sigma_g^+$ states of the Li$_2$ molecule. The data presented here are from Ref. 5. The difference potential, $\Delta V$, is also plotted versus the wavelength scale on the right ordinate.
Fig. 2a. Lowest four electronic states of Na₂. The X 1Σ_g, X 3Σ_u, and a 3Π_u states are reproduced from Ref. 9. The A 1Σ_g state is taken from Ref. 8.
Fig. 2b. Same as Fig. 1b for Na₂. Data from Ref. 8.
Fig. 3. Same as Fig. 1b for $K_2$. Data for the ground state ($X^1\Sigma_g^+$) are taken from Ref. 10. The solid curve A state potential is from the original Morse potential calculated by Loomis and Nusbaum (Ref. 11). However, this curve, when coupled with the accurate X state yields a difference potential giving a satellite at $\sim$1.01 $\mu$m, whereas Sorokin and Lankard (Ref. 13) have observed the satellite to occur in emission at $\sim$1.05 $\mu$m. The dashed-line A state potential is a Morse potential fit to the data of Refs. 11 and 12 but shifted to an $R_e$ of $\sim$4.8 $\text{\AA}$ to obtain a difference potential in agreement with the results of Ref. 13. This is the potential used in the calculations of Fig. 6 and the $K_2$ entries of Table I. The corresponding difference potential is also indicated by a dashed line.
the neighborhood of the potential minimum which dominates the integral if 
\( \beta D_e \gg 1 \) (\( D_e \) is the well depth). The total alkali vapor density \([M_T]\) 
will be in the form of atoms \([M]\), dimers \([M_2]\), and excited states, with 
the latter assumed to be a negligible fraction. Thus:

\[
[M_T] = [M] + 2[M_2] \quad \text{with} \quad [M_2]/[M]^2 = K_X(T). \tag{2}
\]

The resulting concentrations of \( M_2 \) and \( M \) are given in Table I for tem-
peratures which yield total densities of 1 and \( 10 \times 10^{16}/\text{cm}^3 \).

The excited atomic and molecular densities will be a result of competition 
between radiative and collisional rates due to buffer gas, alkali atom, and electron collisions. In the present sec-
tion, we consider the A-X absorption and stimulated emission coefficients 
per \( X \) or A-state molecule for a thermal population of bound states at the 
gas temperature. We then consider the absorption and stimulated emission 
coefficients of the vapor for an assumed \([M_2^*(A^1\Sigma)]/[M_T]\) ratio and the 
equilibrium \([M_2]/[M_T]\) ratio. The appropriateness of these ratios and of 
a thermal bound-state population distribution in the present context is 
considered in the following section.

The averaged absorption and emission coefficients of the alkali 
dimers can be calculated considering the spectrum as a continuum, while 
the results can be understood most easily from a very simple argument. \(^{16}\) 
The A-X transition may be considered to be a resonant oscillator with a 
spontaneous emission rate \( \Gamma \), but with the spectrum broadened across a 
spectral half-width \( \Delta \nu_{1/2} \). Thus, the size of the absorption coeffi-
cient \( \kappa_\nu \) and stimulated emission coefficient \( G_\nu \) are given approxi-
mately by an expression analogous to Doppler broadened lines:
# TABLE I

Specie Concentrations

<table>
<thead>
<tr>
<th>Species</th>
<th>( T ) (K)</th>
<th>( [M_1] )</th>
<th>( K_x )</th>
<th>( K_A )</th>
<th>( [M] )</th>
<th>( K_A[M] )</th>
<th>( [M_2] )</th>
<th>( \frac{[M_2]}{[M_2]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1020</td>
<td>1.0</td>
<td>2.83</td>
<td>47.9</td>
<td>0.95</td>
<td>0.46</td>
<td>0.025</td>
<td>0.201</td>
</tr>
<tr>
<td></td>
<td>1180</td>
<td>10.0</td>
<td>0.595</td>
<td>8.75</td>
<td>9.03</td>
<td>0.79</td>
<td>0.49</td>
<td>0.394</td>
</tr>
<tr>
<td>Na</td>
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<td>1.0</td>
<td>3.35</td>
<td>240.</td>
<td>0.94</td>
<td>2.26</td>
<td>0.03</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>810</td>
<td>10.0</td>
<td>0.71</td>
<td>26.7</td>
<td>8.89</td>
<td>2.37</td>
<td>0.56</td>
<td>0.046</td>
</tr>
<tr>
<td>K</td>
<td>595</td>
<td>1.0</td>
<td>2.14</td>
<td>110.</td>
<td>0.96</td>
<td>1.06</td>
<td>0.02</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>10.0</td>
<td>0.46</td>
<td>14.5</td>
<td>9.23</td>
<td>1.34</td>
<td>0.39</td>
<td>0.072</td>
</tr>
<tr>
<td>Rb</td>
<td>545</td>
<td>1.0</td>
<td>1.5(c)</td>
<td></td>
<td>0.97</td>
<td></td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>645</td>
<td>10.0</td>
<td>0.32(c)</td>
<td></td>
<td>9.43</td>
<td></td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>530</td>
<td>1.0</td>
<td>0.33</td>
<td></td>
<td>0.99</td>
<td></td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>10.0</td>
<td>0.098</td>
<td></td>
<td>9.82</td>
<td></td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>

(a) Alkali vapor pressures from Ref. 15.

(b) Excited molecular A-state fraction necessary for inversion at the satellite wavelength.

(c) Data available for only the bottom quarter of the ground state potential.
\[ \kappa_v = [Na_2] \frac{\lambda^2}{8\pi} (\Gamma/\Delta \nu_{1/2}) \]

\[ G_v = [Na_2^* (A)] \frac{\lambda^2}{8\pi} (\Gamma/\Delta \nu_{1/2}) \]  

\[ k_v = \kappa_v - G_v \]

For a more exact expression we note that the equilibrium populations are radially distributed according to \( d^3 R \exp [-\beta X(R)] \) and \( \nu = A(R) - X(R) \) defines \( R(\nu) \) or \( \nu(R) \), so

\[ \kappa_v = [M_2] \frac{A(\nu)c^2}{8\pi \nu^2} \frac{4\pi R^2}{d\nu/dR} e^{-\beta X[R(\nu)]} \left/ \int_0^\infty d^3 R e^{-\beta X(R)} \right. \]  

\[ G_v = [M_2^* (A)] \frac{A(\nu)c^2}{8\pi \nu^2} \frac{4\pi R^2}{d\nu/dR} e^{-\beta A[R(\nu)]} \left/ \int_0^\infty d^3 R e^{-\beta A(R)} \right. \]  

Here \( A(\nu) = \frac{16\pi^2}{3} \frac{\nu^3}{hc^3} G' D^2 \) is the \( A-X \) transition probability, \( D \) is the dipole moment for radius \( R(\nu) \), \( G' \) is a degeneracy factor equal to 1 for the alkali \( E-E \) transition and \( [M_2^* (A)] \) refers to the total concentration of \( A \)-state molecules. Expressions equivalent to those in Ref. 2 in terms of atomic densities are obtained if

\[ [M_2] \left/ \int_0^\infty d^3 R \exp [-\beta X(R)] \right. = [M_2]/(4 K_A) = [M]^2/4 \]

and

\[ [M_2^* (A)] \left/ \int_0^\infty d^3 R \exp [-\beta A(R)] \right. = [M_2^* (A)]/12 K_A = [M^*][M]/12 \]

from Eqs. (1) and (2) are substituted into Eqs. (4) and (5). In the
present context, however, the molecular densities are more meaningful.

Note that the same \( \exp(-\beta V) \) factors appear in the numerator and denominator of Eqs. (4) and (5), so the potential minima can be defined as the point where \( V = 0 \). With this definition the integrals in Eqs. (4) and (5) depend only on the relative volumes or shapes of the \( A \) and \( X \) potentials, and their ratio \( (A/X) \) is about 2.5:1 for all the dimer cases. Thus from Eqs. (4) and (5):

\[
\frac{G^*}{K} = \frac{[M_2^*(A)]e^{-\beta A(\nu)}}{[M_2^*(A)] e^{-\beta X(\nu)}} = \frac{\frac{-\beta h(\nu - \nu_0)}{[M_2^*(A)] e^{-\beta X(\nu)}}}{[M_2^*(A)] e^{-\beta X(\nu)}} = \frac{-\beta h(\nu - \nu_0)}{[M_2^*(A)] e^{-\beta X(\nu)}}
\]

(6)

where \( A(R) \) and \( X(R) \) are measured from their respective minima and \( h\nu_0 = A(R_{eA}) - X(R_{eX}) \) is the energy separation of the minima. For sodium at 795 nm for example (\( R = 4.35 \, \text{Å} \) in Fig. 2b), the exponential factor in Eq. (6) is \( \sim 80 \) at \( [M_T] = 10^{16} / \text{cm}^3 \) and the requirement for inversion (net gain) is \( [M_2^*(A)]/[M_2] \approx 0.026 \). This required inversion ratio at the satellite is given in Table I for all of the alkali dimers; it is very much higher for the Li case due to the much higher temperature.

The ground state molecular population is always assumed to be maintained at the equilibrium ratio and therefore the absorption coefficient is always given by Eq. (4) with the appropriate \([M_2]\) as given in Table I. These absorption coefficients are given in Figs. 4-6. In order to use Eq. (5) to predict the corresponding stimulated emission coefficient we need \([M_2^*(A)]\). The feasibility of various \([M_2^*(A)]\) values will be discussed in detail in the following section; here we note the essential conclusions and the resultant stimulated emission coefficients.

In the limit of very rapid recombination compared to quenching rates almost all excited alkalis will be in the molecular form since this is
Fig. 4. Stimulated emission and absorption coefficients for Li₂ assuming a total excited species fraction \([M_T^*]\) of 5%, 1/10 of which is assumed to be in the \(A^1Σ_u^+\) state (see text). The two temperatures are indicated by a solid (1020°K) and a dashed (1180°K) line and correspond to \([M_T]\) densities of 1 and \(10 \times 10^{16}\) cm\(^{-3}\), respectively. The molecular transition probability used in the calculation is the calculated value of Tango (Ref. 17) \(\tau = 32.6\) nsec at \(<\lambda^3> = 4.43 \times 10^{-13}\) cm\(^3\)). The right hand ordinate gives the scale for the stimulated emission cross section per excited \(A^1Σ_u^+\) state molecule for the highest temperature. The scale should be multiplied by 10 for the lower temperature. The position of the satellite is indicated by an arrow.
Fig. 5. Same as Fig. 4 for Na$_2$. Again, the calculated value of Ref. 17.
($\tau = 27.3$ nsec at $<\lambda^3> = 3.87 \times 10^{-13}$ cm$^3$) was used, although recent experimental measurements of Baumgartner et al. (Ref. 18) have resulted in a much shorter (12.3 nsec) lifetime of the A state. The net effect of using the experimental lifetime would be to increase the absorption and emission by the same factor.
Fig. 6. Same as Fig. 4 for $K_2$. The technique and calculated dipole moment of Ref. 17 has been used to calculate a lifetime of $\approx 54$ nsec at $\langle \lambda^3 \rangle = 8.85 \times 10^{-13}$ cm$^3$ for use in the calculation.
strongly favored at equilibrium with the buffer gas. These will be distributed between the $^3\Pi_u$, $^1\Sigma_u$, and $^3\Sigma_g + ^1\Pi_g + M^*$ states roughly in the ratio of 6:1:3 so that $M_{2^*}^*(A)/M_T^* \approx 0.1$, where $M^*$ refers to excited atoms, $M_{2^*}^*(i)$ to excited molecules, and $M_T^*$ to all excited species. A 5\% excited-state fraction ($M_{T^*}^*/M_T = 0.05$) is considered feasible and this then yields $M_{2^*}^*(A)/M_T \approx 0.005$ as an upper limit. The stimulated emission coefficients for $M_{2^*}^*(A)/M_T = 0.005$ are plotted in Figs. 4-6 for the Li$_2$, Na$_2$, and K$_2$ cases. We have insufficient information regarding the A-state potentials of Rb$_2$ and Cs$_2$ to include these cases, although we expect net gain at their satellite wavelengths due to the satellite frequency shifts given in Ref. 13. The stimulated emission coefficients in Figs. 4-6 represent upper limits on those obtainable for 5\% excited fraction, but it will be seen in the following section that this is nearly realizable if $^3\Pi_u$ quenching and predissociation is not dominant. The stimulated emission coefficients scale with the excitation fraction and the coefficient per excited molecule, also indicated in the figures, can be used to allow for different $[M_{2^*}^*(A)]$.

As can be seen in Figs. 4-6 the averaged A-X band has a far red edge, and a local maximum just before this edge. In line broadening work such a maximum is called a satellite, and its normal cause is well known. As can be seen in Figs. 1b and 2b the red edge is due to parallel A-state and X-state potentials, which yield a minimum in the difference potential. This satellite and red edge is very prominent in the spectra reported by Sorokin and Lankard.$^{13}$

B. Collision Processes and Radiative Losses

We will consider here a vapor of 1-10 Torr of alkali and 20 atmospheres of noble gas, at a temperature corresponding to this alkali vapor
pressure. These pressure ranges are not chosen by precise optimization; rather the alkali density is in a range where high power laser action appears feasible, and the noble gas density is chosen to be below the maximum that has been used for $\text{Xe}_2$ lasers. The various forms of alkali atoms and molecules will be labeled $M$ for ground (ns) state atoms, $M_2$ for $X^1\Sigma$ state molecules, $M^*_T = M + 2M_2$, $M^*$ for np state atoms, $M_2^*(i)$ for excited molecules in state $i$, and $M_2^* = M^* + \sum_i M_2^*(i)$. The noble gas will be labeled $X$. We assume that a pulsed electron current produces the necessary alkali excitation but that it heats the vapor slowly on the time scale of the present considerations (the magnitudes of this current and the gas, $M_2^*$, and $M_2^*$ vibrational heating rates are discussed in a later section). Some of the processes considered here are also discussed in Ref. 2, and the LiXe-type excimer populations under plasma conditions have been recently modeled.\textsuperscript{19}

To simplify the rate equations, it is useful to first dispense with many of the electron collision processes that do not directly influence the populations of excited alkali dimers. First, we assume that sufficient ionization occurs, possibly e-beam or photoionization sustained, to maintain the necessary electron density in the presence of diffusive loss, recombination, and attachment. The problems involved in operating a pulsed discharge in this medium are not within the scope of this report. Next, we note that below the rare gas ionization threshold the cross section for excitation of the alkali resonance transition is about two orders of magnitude larger than for all inelastic processes with the noble gas.\textsuperscript{20} This very large cross section will tend to maintain low electron energies (<10 eV) at reasonable fields and as a result only alkali excitation, quenching and ionization will occur with significant rates even at
[X]/[M₂] in excess of 10⁴. Furthermore, of all atomic alkali excitation, a large fraction (~98%) goes directly or via ~20 nsec cascading into the resonance level,²¹ while a similarly major proportion of the M₂ excitation should go to the states of the (ns)(np) lowest excited configuration. Thus, only the atomic levels ns and np and the (ns)² and (ns)(np) configurations of M₂ are assumed to be significantly populated and electron excitation to higher levels is ignored.

The dominant collision processes connecting the resonance levels are indicated in Fig. 7a, where electron-collision processes are indicated by wide arrows, buffer gas collisions by narrow arrows, and radiation by wavy arrows. The label R_f refers to three-body recombination or "excimer formation" while R_d refers to dissociation; P and Q refer to electronic excitation and quenching. Estimates of the relative values of these various rates are given for the Na₂ + Xe case with kTe = 0.5 eV, [electrons] = 10¹⁵/cm³, [Xe] = 2 × 10²⁰/cm³, and [Na] = 10¹⁷/cm³. We will discuss these rates in detail below in the process of simplifying Fig. 7a to Fig. 7b which will be used to investigate the feasibility of the system for laser action. Before we become immersed in these details note that in Fig. 7b the basic process is electron excitation of M* followed by recombination into the a³Π_u and a¹Σ_u states of M₂*. These two states are strongly coupled by electron spin exchange collisions and in addition they should be formed approximately in the ratio of their statistical weights. We thus assume that the result is an a³Π_u/a¹Σ_u population ratio of 6:1 (the ratio of their statistical weights). We refer below to the sum of these a³Π_u and a¹Σ_u populations, in a 6:1 ratio as M₂* or M₂*(a³Π_u + a¹Σ_u). The population of this coupled pair of states is lost through electron and X quenching to the x³Σ_u state, and pos-
Fig. 7a. Estimated dominant collisional and radiative rates for a vapor of \([\text{Na}] = 10^{17}/\text{cm}^3\) and \([\text{Xe}] = 2 \times 10^{20}/\text{cm}^3\). Electron collision processes are labeled with wide arrows, gas collision processes by narrow arrows, and radiative processes by curved arrows. The indicated energies of \(\text{Na}_2\) states on the left are representative of the order only. The estimated rates are given in units of \(10^8/\text{sec}\) in parentheses.
\[ [X_e] = 2 \times 10^{20} \text{ /cm}^3 \]
\[ [\text{Na}] = 10^{17} \text{ /cm}^3 \]
\[ [e^-] = 10^{15} \text{ /cm}^3 \]

**Fig. 7b.** Effective collisional and radiative rates for the Na + Xe\(^*\) electron plasma in Fig. 7a, after the simplifications described in the text. The \( M_2(\alpha^{3}\Pi_u + A^{1}\Sigma_g^+) \) "state" represents a statistical 6/1 mixture of \( \alpha^{3}\Pi_u \) and \( A^{1}\Sigma_g^+ \) states. The general alkali notation of Eqs. (4) and (5) is used, although \( M \) represents the Na case for the indicated rates.
sibly by predissociation of \( a^3\Pi_u \). If predissociation occurs it is much faster than all other processes and, due to the \( A^1\Sigma_u^+ - a^3\Pi_u \) collisional coupling, the \( A^1\Sigma_u^+ \) population will have no chance of reaching threshold for laser action; nor could efficient energy conversion occur if \( A^1\Sigma_u^+ \) and \( a^3\Pi_u \) were only weakly coupled. The evidence regarding \( a^3\Pi_u \) predissociation is discussed in Appendix A. Here we will assume that rapid predissociation does not occur since this is supported by the available evidence and this entire exercise is irrelevant otherwise.

The next simplification is to consider the populations of rotational-vibrational states to be in a thermal distribution at the gas temperature. Thus, only the total populations of each molecular electronic state will be considered as a variable. This necessary simplification is expected to be a reasonable approximation since the rotational and vibrational relaxation rates due to X collisions should be faster than all other collisional and radiative rates, even after allowing for the probable transfer of only a small fraction of the binding energy per X collision. If more than twenty X collisions are required to thermalize the strongly bound \( A^1\Sigma_u^+ \) and \( a^3\Pi_u \) states, their populations might be at somewhat elevated temperatures. If the effective temperature is a few times the gas temperature this will conveniently yield more optical gain near the A-X satellite.

The equilibrium ratio, \([M_2^*(\text{state } i)])[M^*] = [M]K_i(T) = R_f/R_d\), where \( T \) is the gas temperature, is a useful parameter since it establishes the maximum \([M_2^*(\text{state } i)])[M^*] \) ratio achievable at high \([X]\) as well as the ratio of excimer formation \( R_f \) to destruction \( R_d \) rates due to X collisions. From the potentials in Figs. 1-3 and Eq. (2) one finds that the \( B^1\Pi_u \) equilibrium ratios \([M_2^*(B)])[M^*] \) are quite small, as is
the $^{1} \Sigma^{+}_{u}$ ratio for the Li$_2$ case. All of the A-state ratios are given in Table I (as $[M]K_A$), as well as can be done with present knowledge of the potentials. The fact that these $M_2^*(A)/M^*$ equilibrium ratios exceed 1, except for Li, allows the possibility of converting a large fraction of the electron-excited $M^*$ population into $M_2^*$ by X collisions. The equilibrium molecular ratios for the $a^3 \Pi_u$ state greatly exceed those for the A states due to the deeper binding and a statistical factor of six. Thus, in the non-equilibrium situation, the dominant effect of X collisions on excited state populations is to cause excimer formation $[M^* + M + X \rightarrow M_2^*(A^1 \Sigma^{+}_{u} + a^3 \Pi_u) + X]$ and relaxation of the $M_2^*(A^1 \Sigma^{+}_{u} + a^3 \Pi_u)$ vibrational and rotational populations toward an equilibrated distribution; dissociation of these two states by X collisions is quite minor.

It is convenient to consider the electron energy distribution to be Maxwellian and characterized by an electron temperature, $T_e$ (see Ref. 2). Under this assumption, the ratio of the excitation ($P$) to quenching ($Q$) rates is given by thermodynamics as $P/Q = (g^*/g) \exp(-\Delta E/kT_e)$, where $\Delta E$ is the excitation energy. If electron collision rates dominate, the ratio of excited to unexcited species is given by the same factor. In Ref. 2 $kT_e \approx 0.35$ eV, corresponding to 1.4% excited Li, was assumed to be realizable, based on steady-state plasma studies. For the pulsed discharge or e-beam excitation considered here much higher effective temperatures should be possible, and we will consider here the consequences of $kT_e$ in the range 0.3–3 eV. As noted above, the ratios $P/Q$ in Figs. 7a and 7b correspond to 0.5 eV for the sodium case. The effective radiation decay rate for $M^*$ is less than 1% of the natural decay rate due to radiation trapping. This is insignificant compared to the other rates in Fig. 7 and is deleted.
As indicated in Fig. 7a, we assume that the electron quenching rates are the same for the molecular and atomic excited states. For the X ↔ A, X ↔ B, and M ↔ M\textsuperscript{*} cases this assumption is based on the similarity in energies, dipole moments, and electron orbit diameters. The \( a^3\Pi_u \rightarrow x^3\Sigma_u \) transition is optically forbidden, but near threshold the cross section should be large and in the absence of data we assume the same rate as for the dipole transitions. Due to the small \( M_2/M \) fraction, most of the \( a^3\Pi_u + a^1\Sigma_u^+ \) population (\( M_2^* \)) is due to atomic excitation followed by recombination; the direct \( M_2 \rightarrow M_2^* \) excitation should typically yield an additional 10-20% contribution to this excitation rate. The quenching of \( a^1\Sigma_u^+ \) and \( a^3\Pi_u \) to \( x^3\Sigma_u^+ \) should add a similar fraction to the quenching via \( x^3\Sigma_u \). These two small opposite corrections are deleted from Fig. 7b in the interest of simplicity.

Electron collisions with \( a^1\Sigma_u^+ \) and \( a^3\Pi_u \) will fairly efficiently excite molecular levels with energies up to \( kT_e \) above these levels. Excitation of states of higher configurations and dissociating states of the (ns)(np) configuration require more than 1 eV and will only be important at the highest \( kT_e \) considered. Such excitations have a high probability of cascading into \( A^1\Sigma_u^+ + a^3\Pi_u \) or dissociating to \( M^* \) and recombining back into \( A^1\Sigma_u^+ + a^3\Pi_u \). Thus these excitations result in a minor source of gas heating and a small decrease in \( M_2^* \) population. At the lower \( kT_e \), where it is more difficult to achieve threshold for laser action, only the \( b^1\Pi_u \) and \( b^3\Sigma_g \) states can be excited from \( a^1\Sigma_u^+ \) and \( a^3\Pi_u \) at significant rates.

As indicated in Fig. 7a, these B states should generally be quenched back to \( A^1\Sigma_u^+ + a^3\Pi_u \) before dissociating to \( M + M^* \). The net result, as shown in Fig. 7b, is a minor contribution \( P_d \) to the dissociation rate and additional \( a^3\Pi_u - A^1\Sigma_u^+ \) coupling. The excitation of dissociating states at higher \( kT_e \)
can be considered to be an increase in \(P_d\); as can be seen from Fig. 7b, this is unlikely to be of much consequence compared to quenching. The rather large \(b^3\Sigma_u \rightarrow a^3\Pi_u\) and \(B^1\Pi_u \rightarrow A^1\Sigma_u^+\) quenching rates due to \(X\) collisions in Fig. 7a are not very important, but are assumed to be this large since the states are mixed by a long range rotational interaction. Compensating statistical and symmetry factors lead us to the same estimate for both quenching rates. The rate coefficients used in Fig. 7 are listed in Table II.

The success of this laser system depends critically on the excimer recombination rate constant \(k_f\) for \(M^* + M + X \rightarrow M_2^* + X\), and on the quenching rate constant \(k_q\) for \(M_2^*(A^{1\Sigma_u^+} + a^3\Pi_u) + X \rightarrow M_2(x^3\Sigma_u) + X\). Neither rate can be easily estimated from known rates, so we consider them in detail in Appendix B. The results from this appendix are given in Table II and in Figs. 7a and 7b as \(R_f\) and \(R_q\).

C. Threshold Condition

From Fig. 4b, the rate equations for the excited atomic \((M^*)\) and \(A^{1\Sigma_u^+} + a^3\Pi_u (M_2^*)\) populations are:

\[
[M^*] = P[M] - [M^*](Q + R_f) + [M_2^*](P_d + R_d)
\]

\[
[M_2^*] = R_f[M^*] - [M_2^*](R_{eff} + Q' + R_q + P_d + R_d)
\]

The solution of these coupled linear homogeneous equations for an excitation, \(P\), that is switched on is straightforward but unnecessary. It is sufficient to note that the \([M_2^*](Q + R_d)\) term in Eq. (7) is a minor correction, so that Eq. (7) yields:

\[
\frac{[M^*]}{[M]} \approx \frac{P}{Q + R_f} \left[1 - e^{-(Q + R_f)t}\right]
\]


TABLE II

Rate coefficients assumed for Na + Xe with \( kT_e = 0.5 \) eV and \( T_{\text{gas}} = 810^\circ \text{K} \).

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate Coefficient</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e^- + \text{Na}(3p) \rightarrow e^- + \text{Na}^*(3p) )</td>
<td>( 2 \times 10^{-7} ) cm(^{3}/s )</td>
<td>Ref. 14. Almost independent of ( T_e ).</td>
</tr>
<tr>
<td>( e^- + \text{Na} \rightarrow e^- + \text{Na}^*(3p) )</td>
<td>( 1 \times 10^{-8} ) cm(^{3}/s )</td>
<td>Ref. 14. Varies as ( \exp(-2.1 \text{ eV}/kT_e) ).</td>
</tr>
<tr>
<td>( e^- + \text{Na}_2^<em>(2) \rightarrow e^- + \text{Na}_2^</em> )</td>
<td>( 2 \times 10^{-7} ) cm(^{3}/s )</td>
<td>rough guess</td>
</tr>
<tr>
<td>( e^- + \text{Na}_2^<em>(1) \rightarrow e^- + \text{Na}_2^</em> )</td>
<td>( g_j \times 7 \times 10^{-8} ) cm(^{3}/s )</td>
<td>rough guess</td>
</tr>
<tr>
<td>( \text{Na}(3p) + 2 \text{Xe} \rightarrow \text{NaXe}(A^{1\Sigma_u^+} + a^{3\Pi_u}) + \text{Xe} )</td>
<td>( 8 \times 10^{-30} ) cm(^{6}/s )</td>
<td>Appendix B</td>
</tr>
<tr>
<td>( \text{NaXe}(A^{1\Sigma_u^+}) + \text{Xe} \rightarrow \text{Na} + 2 \text{Xe} )</td>
<td>( 4 \times 10^{-14} ) cm(^{3}/s )</td>
<td>Appendix B</td>
</tr>
<tr>
<td>( \text{Na}_2(B^{1\Sigma_u}) + \text{Xe} \rightarrow \text{Na}_2(A^{1\Sigma_u}) + \text{Xe} )</td>
<td>( 2.5 \times 10^{-12} ) cm(^{3}/s )</td>
<td>rough guess</td>
</tr>
<tr>
<td>( \text{Na}_2(b^{3\Sigma_g}) + \text{Xe} \rightarrow \text{Na}_2(a^{3\Pi_u}) + \text{Xe} )</td>
<td>( 2.5 \times 10^{-12} ) cm(^{3}/s )</td>
<td>rough guess</td>
</tr>
<tr>
<td>( \text{Na}_2(a^{3\Pi_u}) + \text{Xe} \rightarrow \text{Na}_2(x^{3\Sigma_u}) + \text{Xe} \rightarrow \text{Na} + \text{Na} + \text{Xe} )</td>
<td>( 2.5 \times 10^{-14} ) cm(^{3}/s )</td>
<td>very uncertain and crucial! Appendix B</td>
</tr>
</tbody>
</table>
Then, substitution of Eq. (9) into Eq. (8) yields:

\[
\frac{[M_2^*]}{[M]} \approx \frac{R_f}{\Gamma_{\text{eff}} + Q' + R_q + P_d + R_d} \cdot \frac{P}{Q + R_f} \left[ (1-e^{-at}) - \alpha \left( \frac{e^{-at} - e^{-\beta t}}{\beta - \alpha} \right) \right]
\]

(10)

where \( \alpha = \Gamma_{\text{eff}} + Q' + R_q + P_d + R_d \) and \( \beta = Q + R_f \). The second term in parentheses in Eq. (10) is just a brief transient that holds down \([M_2^*]\) momentarily due to the necessity of populating \(M^*\) before starting to populate \(M_2^*\). The basic time dependence is a buildup of \(M^*\) at the inverse of its relaxation rate \(\beta\) and a buildup of \(M_2^*\), after a brief delay, at the inverse of its relaxation rate \(\alpha\). From Fig. 7b it can be seen that we expect \(\alpha^{-1} \approx 3\) nsec, \(\beta^{-1} \approx 2\) nsec. Thus the steady-state populations are reached in this case in \(\sim 10\) nsec, and if the pumping rate is not constant after being switched on, the populations respond with a \(\sim 4\) nsec time constant. A faster response is obtained at higher electron densities and vice versa, as discussed below.

From Table I, the threshold condition for net gain in the Na\(_2\) and K\(_2\) cases at \([M_1]\) = 10\(^{17}\)/cm\(^3\)) is \([M_2^*]/(A_u^{1\Sigma^+} \text{only})]/[M_2] \approx 0.06\) or \([M_2^*]/[M_2] \approx 0.4\), where \([M_2^*]\) means total \(a_{1\Pi_u} + A_{1\Sigma^+}^1\) with a 6 to 1 ratio of population. Also, from Table I, \([M_2]/[M_T] \approx 0.05\) for these cases. Combined with Eq. (10) these data yield the condition for net gain:

\[
\frac{R_f}{\Gamma_{\text{eff}} + R_q + Q'} \cdot \frac{P}{Q + R_f} \approx \frac{[M_2^*]}{[M_1]} = \left( \frac{[M_2^*]}{[M_2]} \right) \left( \frac{[M_2]}{[M_T]} \right) \geq 0.4 \cdot 0.05 = 0.02 \quad , (11)
\]

where we have approximated \(\alpha\) as \(\Gamma_{\text{eff}} + R_q + Q'\) since \(P_d << Q'\) at all electron densities and \(R_d < R_q\) at all \([X]\). The expression \(PR_f/(R_f + Q)\) is the effective pumping rate and \(\Gamma_{\text{eff}} + R_q + Q'\) the relaxation rate for \([M_2^*]\). \(P, Q,\) and \(Q'\) are proportional to electron density, \(R_f = k_f[M][X]\),
and \( R_q = k_q[X] \). The electron excitation and quenching rates \( P \) and \( Q \) are well known, and \( Q' \approx Q \) appears to be a reasonable assumption. Thus, \( R_f \) and \( R_q \) or \( k_f \) and \( k_q \) are the only crucial rates, other than predissociation, which are very difficult to estimate. For this reason we have discussed them in detail in Appendix B.

Equation (11) is just satisfied by the rates given in Fig. 7b for \( \text{Na}_2 \), corresponding to \( kT_e = 0.5 \) eV. Note, however, that as \( kT_e \) is raised, \( P \) increases as \( \exp(-2.1 \text{ eV/kT}_e) \), while all the other rates remain essentially unchanged. Also, \( R_f \) could be raised by increasing \([X]\) and the ratio in Eq. (11) can be optimized at a larger value if the electron density is lower. Thus, \( kT_e \geq 0.5 \) eV is an approximate threshold requirement for the \( \text{Na}_2 \) case and if only the rate constants are considered, one might expect this threshold \( kT_e \) to scale roughly in proportion to the atomic excitation energies for \( \text{K}_2 \), \( \text{Rb}_2 \), and \( \text{Cs}_2 \). Unfortunately, the \( \text{A-} \) state potentials are so poorly known for \( \text{Rb}_2 \) and \( \text{Cs}_2 \) that the threshold ratio of \([M_2]^*[(\text{A}^1\Sigma_u^+)]/[M_2]\) is very uncertain in these cases. There appears to be little hope for laser action in \( \text{Li}_2 \) because the \( \text{A}^1\Sigma_u^+ \) state is dissociated rapidly by \( X \) collisions (the equilibrium fraction \([\text{Li}_2^*[(\text{A}^1\Sigma)]/[\text{Li}^*] \) is less than 1).

The electron densities and currents necessary to produce the \( P = 0.15 \times 10^8/\text{sec} \) rate in Fig. 7 are discussed below in a separate section. Note that raising the electron density beyond this value causes the left side of Eq. (11) to approach \( (P/Q)(R_f/Q') \), while lowering the electron density causes an approach to \( P/(\Gamma_e + R_q) \). The laser threshold condition requires slightly higher \( kT_e \) in the former and lower \( kT_e \) in the latter case (the assumption of \( [a^3\Pi_u]/[\text{A}^1\Sigma_u] = 6/1 \) breaks down at low electron densities). From the standpoint of efficiency, it is
important to note that the $M^*$ quenching associated with the Q term causes no net energy loss, whereas the $Q'$ and $R_q$ quenching transfers typically 1 eV into gas heating. Of course, if this medium were used as a gain cell or self oscillator the stimulated emission rate could compete efficiently with these quenching loss rates at high powers.

D. Electron Currents and Energy Deposition

At electron energies above 100 eV, the alkali resonance line excitation cross section has about the same energy dependence as the alkali and rare gas ionization cross sections. The resonance line cross section (15 Å$^2$ at 100 eV) is about a factor of 10 greater than for alkali ionization, and about a factor of 100, 15, 6, 4, 3 greater than for ionization of He, Ne, Ar, Kr, Xe, respectively. Thus, at the proposed rare gas/alkali density ratios of $\sim$1000/1, most collisions above 100 eV will go into ionization of the noble gas. The ionization cross sections drop rapidly with decreasing energy at energies below about twice threshold (30-50 eV). The alkali excitation cross sections, on the other hand, peak at about 10 eV (with a value of $\sim$40 Å$^2$) and are still quite large at 3 eV. Thus there is a cross-over energy, in the neighborhood of 20 eV, below which the alkali excitation dominates the electron energy deposition.

For high energy (e-beam) electron collisions, the secondary electrons from xenon ionization with energies, $E$, below $\sim$15 eV will cause predominantly alkali excitation, while secondaries with $E > 15$ eV will primarily induce further ionizations. Thus in the Xe case, for which the mean energy of secondaries with $E < 15$ eV is about 6 eV$^{22}$ and the ionization energy is 12 eV, the average energy transferred to the electrons that cause alkali excitation is 18 eV (12 eV + 6 eV). Once the energy
of these $E < 15$ eV secondaries falls below 2 eV they can no longer excite
the alkali, so that only 4 eV of the 6 eV average energy is useful. This
yields an energy efficiency factor of 4/18 or $\sim$20% for e-beam energy depo-
sition. The $Xe^+$ which result from these ionizations are expected to form
$Xe_2^+$, then $Xe_2^*$ and $Xe^*$ with radiative energy loss as in the $Xe_2$ laser
systems.\footnote{23} If $Xe_2^*$ or $Xe^*$ collide with M before they radiate, some of
the $Xe$ ionization energy may eventually produce additional $M_2^*$, but at
$[M] = 10^{17}/cm^7$ the radiative loss occurs much more rapidly than M col-
lisions. Thus, the $X$ ionization energy is largely lost as far as alkali
excitation is concerned and the above $\sim$20% maximum energy efficiency
factor is appropriate. For this reason, pure e-beam excitation is not
recommended for either alkali dimer or alkali-noble gas laser systems.

Acceleration of low energy electrons by an externally applied field should
be used for most of the energy deposition, perhaps with photoionization
or e-beam preionization or sustaining. Under these conditions, almost
all electron energies will be below 10 eV and almost all of the electrical
energy will go into alkali excitation.

The electron collisional de-excitation rate constants for the Li and
Na resonance transitions are about $2 \times 10^{-7} \ cm^3/sec$ for electron tempera-
tures between 0.3 and 10 eV, while the rates for K, Rb, and Cs are expected
to be slightly greater.\footnote{21} Thus the quenching rate $Q = 3 \times 10^{8}/sec cor-
responding to the $\sim$5 nsec response case considered in Fig. 7 requires an
electron density of about $10^{15}/cm^3$. The rate of energy-deposition into
$M^*$ energy of $P[M]dE$ is then about 500 MW/$l$ and an excitation energy density
of $\sim$$2J/l$ at $[M^*_T]/[M_T] = 0.05$ is reached in $\sim$5 nsec. The corresponding
$kT_e \approx 0.5$ eV current density is in the neighborhood of 30 $A/cm^2$. If the
electron density and rates in Fig. 7 are a factor of 20 smaller, the laser
threshold condition is still satisfied, while the \( \sim 2J/\ell \) excitation energy and laser threshold is reached in \( \sim 100 \) nsec. Further lowering the electron density requires \( kT_e > 0.5 \) eV to satisfy the threshold condition.

E. Gas Heating and Laser Efficiency

One form of gas heating by electrons will be via vibrational and rotational excitation of \( M_2^* \), \( M_2^* \) and \( MX^* \) followed by rapid cooling via X collisions. Rate constants for such collisions are usually \( 10^{-8} \) cm\(^3\)/sec or less but might be somewhat larger in the resonance region for these larger \( Na_2 \) and \( Na_2^* \) molecules. If we assume \( 10^{-8} \) cm\(^3\)/sec this is the same as the \( M \rightarrow M^* \) excitation rate for the \( kT_e \approx 0.5 \) eV threshold condition. The average energy transfer in vibrational and rotational excitation will be \( 5kT_e \), whereas the \( M \rightarrow M^* \) excitation energy is \( \sim 4 \) kT\( e \).

Since the ratio \( ([M_2] + [M_2^*] + [MX^*])/[M] \) is less than 0.1, the energy deposition rate into vibrational heating would be less than 2\% of the rate into alkali electronic excitation and is negligible.

The difference between the \( M^* \) excitation energy \( h\nu_o \) and laser photon energy \( h\nu_x \) goes directly into gas heating, yielding an efficiency factor \( \nu_x/\nu_o \) of typically 70\%. The mechanisms by which this heats the gas are the recombination into and vibrational relaxation of \( M_2^* (A^1\Sigma_u + a^3\Pi_u ) \). The radiative transition to vibrationally excited states of \( X^1\Sigma_g^+ \) with subsequent relaxation by X collisions is in fact exceeded by a gas cooling effect of \( X^1\Sigma_g^- \) dissociation to maintain the equilibrium molecular fraction; the net result is the above \( \nu_x/\nu_o \) factor. It is important to note that if dissociation from \( X^1\Sigma_g^- \) is not sufficiently rapid to maintain the equilibrium \( M_2/M \) ratio, the net optical gain should improve. The increased \( M_2 \) absorption is more than
compensated by the additional $M_2^*(A^1Σ_u^+)$ population due to electron excitation of $A^1Σ_u^+$ from $X^1Σ_g^+$.

The collisional quenching of $M_2^*(A^1Σ_u^+ + a^3Π_u)$ to $X^3Σ_u^+$ at a rate $R_q^0 + Q'$ puts most of the $M_2^*$ excitation energy into gas heating (see Fig. 7b). This quenching rate plus the $Γ_{\text{eff}}$ spontaneous emission rate are the primary loss mechanisms competing with the stimulated emission rate $Γ_s$ (neglecting predissociation). The ratio of this $R_q^0 + Q' + Γ_{\text{eff}}$ loss rate to the $Γ_s$ laser emission rate largely determines the laser efficiency as a fraction of $ν_\lambda/ν_o$. The size of $Γ_s$ is determined by the necessity of satisfying the threshold condition, Eq. (11), with $Γ_s$ added to the $Γ_{\text{eff}} + R_q^0 + Q'$ denominator. When the threshold condition is barely satisfied most of the electrical energy will be going into gas heating. As the excitation fraction increases beyond the threshold condition in Eq. (11) additional energy is available for laser power. As an example, if the $kT_e \approx 0.5$ eV threshold condition of Sec. II C is increased to $kT_e = 0.67$ eV Eq. (11) is exceeded by a factor of three, two-thirds of which is available for laser power. The overall electrical efficiency would then be ~50%.

For the conditions assumed in the above discussions, a significant and sometimes major fraction of $[M_T^*]$ is not in the $M_2^*(A)$ form which contributes to the laser energy. For long laser pulses, much of the $M^* + M_2^*(a^3Π_u)$ stored energy can feed $Na_2^*(A)$ while it is being depleted by laser action, but for near-threshold and short-pulse operation much of this excitation energy is unavailable as laser energy.

The gas temperature rise due to gas heating without conductive cooling can be estimated for the above 50% electrical efficiency case, for which half of the excitation energy goes into gas heating and half
into laser energy. This will yield a heating power equal to the
laser power, and for a specific heat of $\sim 10 \ J/\ell^\circ C$ at $[X] = 2 \times 10^{20}/cm^3$
this will yield a heating rate of $0.1^\circ C$ per $J/\ell$ of laser power. For the
high electron density system considered above this energy deposition
occurs in a few nanoseconds, so the gas temperature would rise several
hundred degrees and destroy the gain inversion after $\sim 10 \ \mu sec$. This
appears to be the primary constraint on total pulse power or duration.
However, the assumption of insignificant temperature rise during the $M^*$
and $M_2^*$ relaxation times used in the previous section is well justified;
the temperature rise over this time period is $\sim 0.1^\circ C$. Gas heating due
to elastic electron collisions with $X$ should make a negligible addition
to this heating rate.
III. LOW-DENSITY LASER SYSTEM

We will now consider operation at sufficiently low [X] and [M] to leave the discrete lines of the A-X band essentially unBroadened. The overall intensity pattern of the absorption coefficient is the same under these conditions, but it is in the form of discrete lines with an average spacing of about 1 cm$^{-1}$ between strong lines. The Doppler width is about 0.04 cm$^{-1}$ so the absorption coefficient is typically 25 times greater in the strong lines than for the continuum in Figs. 5-7, since $\int k_v dv$ over the entire band is unchanged. The emission band is similarly in the form of discrete lines with typically 25 times the gain that might be inferred from Figs. 4-6, but in this case the band shape is in general not the thermal shape of Figs. 4-6. Under these low-density conditions, the only appreciable source of $M_2^*(A)$ is via electron excitation of $M_2(X)$. The excitation process is approximately governed by the classical Franck-Condon principle of $\Delta R = 0$, nuclear kinetic energy conserving excitation, so $M_2^*(A)$ vibrational states with inner turning points near $R_{eX}$ are strongly favored in the excitation. Fluorescence from these vibrational states will strongly favor photon energies corresponding to $V_A-V_X$ at their outer turning point radii. It can be seen in Figs. 1-3 that the outer turning points for these vibrational states are near the satellite radius, so that the major fraction of the emission will be concentrated near the satellite. This can be seen in the low-pressure discharge spectra given by Sorokin and Lankard, and it is also quite similar to the well-known $H_2$ laser of Ref. 1. Many lines will be closely packed in this satellite region so that the above factor of 25 in gain compared to Figs. 4-6 will be much smaller here. However, in the sense of Eq. (4) or, $\int G_v dv$ being conserved, this narrowed emission band will have additional gain per $M_2^*(A)$
in the satellite region.

There are, however, some complications of this low-pressure laser system. One problem, which might be cured by a buffer gas or alkali density of \( \sim 10^{18} \text{ cm}^{-3} \), is the absence of homogeneous broadening. The \( M_2^*(A) \) in a given vibrational and rotational state can only radiate into the lines originating in that state since there is negligible collisional mixing within the lifetime or laser pulse time. Thus, unless some \( 10^{18} \text{ cm}^{-3} \) of \( M \) or \( X \) is available to cause vibrational and rotational transitions only the populations associated with lasing lines will contribute. In addition a multi-lined band and other undesirable features of inhomogeneous broadening will occur. Another issue is the vibrational heating of \( Na_2 \) with the associated spreading out of the absorption band and increasing absorption in the satellite region. The heating rate of 0.1°C per J/\( \ell \) of laser energy calculated for \( [X] = 2 \times 10^{20} \text{ cm}^{-3} \) becomes about 2000°C per J/\( \ell \) for unbuffered Na vapor at \( [Na] = 10^{16} \text{ cm}^{-3} \). Thus buffer gas would again be needed to achieve much more than 0.05 J/\( \ell \) in a single pulse. Typical non-resonant collisional line broadening reaches 0.02 cm\(^{-1}\) at \( \sim 2 \times 10^{18} \text{ cm}^{-3} \) so this much buffer gas could probably be introduced without significantly broadening the lines and causing loss of gain. Thus, these disadvantages could probably be overcome with something like a He buffer gas density of about 50 Torr and still leave the possibility of discharge type operation.

There is, however, a serious problem with the efficiency of this low-pressure system. The fraction \( [M_2]/[M_T] \) is less than 0.03 for the various alkalis at \( [M_T] \leq 10^{16} \text{ cm}^{-3} \) (Table I) and even smaller \( [M_T] \) may be necessary to avoid superradiance. The cross section for electron excitation of \( M_2 \) to \( M_2^*(A) \) is at best equal to that for \( M \rightarrow M^* \), so the major proportion of the electrical excitation will be of \( M^* \) rather than \( M_2^* \). When electron
collision rates dominate over radiative rates, the ratio of energy stored
in $M^{*}$ versus $M_2^{*}(A)$ will be about 3 times $[M]/[M_2]$ due to the statistical
factor, and when stimulated or spontaneous radiative losses are considered
the $[M^*]/[M_2^*]$ ratio is even larger. Since only $M_2^*(A)$ can contribute to
the laser energy this $M^*$ excitation with $[M^*]/[M_2^*(A)] \geq 100$ represents a
major energy drain for pulsed operation. The microsecond times for dif-
fusive loss of $M^*$ radiation would yield a low energy-loss rate due to $M^*$
once the equilibrium value $[M^*]/[M] = P/Q$ was established in a time of
$Q^{-1}$. During a long pulse, $M_2^*(A)$ might be usefully contributing laser
power over many A-state relaxation times. Then the $M^*$ stored energy that
is initially lost might not be such a large fraction of the total electro-
cal energy input since the $[M^*]$ was static for much of the laser period.
The $M_2$ vibrational heating issue must, of course, be re-examined in this
case since net gain can be lost due to gas heating. If cw operation is
considered, the gas heating is the paramount consideration.

It appears, therefore, that the unbuffered or low buffer-gas density
system might make a feasible laser, with the possibility of discharge type
operation at much lower $[M]$ and $[X]$ than for the high $X$ pressure system.
However, the efficiency and particularly the high-power aspects of the
high-pressure system appear much more promising.
IV. INFLUENCE OF ALKALI DIMERS ON ALKALI-NOBLE GAS LASER ACTION

The possibility of "excimer" laser action due to the A-X system of the alkali-rare gas molecules, particularly LiXe, was suggested by Phelps. A major loss mechanism for such systems is absorption by the alkali dimers, which may exceed the net gain due to LiXe for the conditions suggested in Ref. 2. Furthermore, because of the very high gas densities involved, the M₂ absorption spectrum will be a continuum (as assumed for Figs. 4-6) without the gaps usually associated with bound-bound spectra. The situation is illustrated for the Na case in Fig. 8. Here we have utilized the quasi-static theory and an assumed [Na⁺]/[Na] ratio of 5% to calculate the stimulated emission and absorption coefficients²,⁴ for the Na-Xe molecule using recently measured spectra and inferred potential curves.²⁴ These coefficients have been expressed in units of absorption and emission per cm of path length in the medium. For comparison, we have plotted the Na₂ absorption coefficient for the same conditions. Clearly, the dimer absorption dominates the spectrum and renders the Na-Xe system hopeless under these conditions.

There are a number of ways in which this difficulty might be overcome. The "excimer" stimulated emission coefficient scales directly with the excited fraction and with the Xe density; an improvement in the combination of these two might bring the gain to the point where it could compete with the M₂ absorption.

Another approach is to heat the gas without raising the alkali vapor pressure. From Eq. (4) and the conversion from [M₂] to [M]² given below Eq. (4), one can see that the absorption coefficient varies as [M]² \exp(-X[R(λ)])/kT) where X(R) is the X¹Σ state potential relative to X(∞). At λ ≈ 690 nm, corresponding to optimum NaXe gain in Fig. 8, X[R(λ)] is
Fig. 8. Comparison of Na-Xe stimulated emission and absorption coefficients\textsuperscript{24} with the Na\textsubscript{2} dimer absorption coefficient for conditions indicated. The Na\textsubscript{2} absorption coefficient is calculated based on the arguments of Section II, while the Na-Xe coefficients are based on arguments similar to those of Ref. 2.
about -5500 cm$^{-1}$ (see Fig. 2b). Thus the Na$_2$ absorption in this wavelength region varies as [Na]$^2$ exp(5500 cm$^{-1}$/kT). The NaXe A-state potential is about -1000 cm$^{-1}$ at the radius responsible for the 690 nm emission, so the NaXe* stimulated emission coefficient varies as [Na*][Xe] exp(1000 cm$^{-1}$/kT). The ratio of NaXe* stimulated emission to Na$_2$ absorption at $\lambda \approx$ 690 nm and constant [Na], [Na*], and [Xe] thus varies as exp(4500 cm$^{-1}$/kT). For example, a change from the T = 700$^\circ$K of Fig. 8 to T = 900$^\circ$K decreases the Na$_2$ absorption relative to the NaXe stimulated emission by a factor of 8. The NaXe $^2$X-state absorption also increases due to the exp[$-^2X(\lambda)/kT$] factor, but the net result is a change in Fig. 8 that yields net gain in the 690-710 nm region.

Another possibility is that at very high rare-gas densities ($\sim 10^{21}$/cm$^3$) the MX$_n$* spectrum with $n \geq 2$ will spread beyond the $M_2$ absorption satellite. Net gain is virtually certain at such wavelengths, the question is if sufficient gain can be achieved to overcome optical losses.

The alkali-dimer absorption will decrease rapidly beyond the wavelength of the red satellite, which is known experimentally from the measurements of Sorokin and Lankard$^{13}$ for the Na, K, Rb and Cs cases and can be calculated for the Li case from measured potentials.$^5$ In all Li, Na, Rb, and Cs cases except CsHe, RbHe, LiHe, and LiXe our measurements indicate that the wavelength region where alkali-rare gas laser action can be expected is of shorter wavelengths than the $M_2$ satellite. In the CsHe and RbHe cases we do not know how far the MX* stimulated emission extends to the red, since our measurements did not extend to long enough wavelengths. In the LiHe and LiXe cases our measured emission spectrum extended beyond the $M_2$ red edge at 900 nm.$^{25}$ Thus the $M_2$ absorption represents a severe
drawback for all but these excepted cases and perhaps for the CsHe and RbHe cases as well. In Ref. 2, theoretical potentials by Baylis were used to model the LiXe system, and maximum gain was found to occur at ~950 nm, beyond the Li₂ satellite at 900 nm. We find that the maximum gain actually occurs near 890 nm, but about 1/3 as much gain is still left at 920 nm, well beyond the Li₂ red absorption edge or satellite. Thus the LiXe laser system considered in Ref. 2 still looks promising.

Even if there were no absorption due to Li₂ at λ > 900 nm, the Li₂ can affect the efficiency with which the LiXe system can operate. The Li₂(3P_u) state has an equilibrium fraction much greater than unity and hence constitutes a drain of the Li⁺ and thereby the LiXe⁺ population. If the Li₂⁺(3P_u) predissociates, this recombination will be a continuous Li⁺ (and hence energy) loss mechanism; otherwise, the 3P_u state will absorb Li⁺ at its recombination rate R_f until the steady-state [Li₂⁺(3P_u)]/[Li⁺] fraction is attained. Electron collisions, as considered in Fig. 4, should hold this fraction below the equilibrium fraction, but this inaccessible stored excitation energy can have a significant effect on overall pulsed-laser efficiency. For the conditions suggested in Ref. 2 ([Li] = 3 \times 10^{-16} / \text{cm}^3, [Xe] = 10^{20} / \text{cm}^3), the 3P_u recombination rate coefficient of ~5 \times 10^{-30} \text{cm}^6 / \text{sec} estimated in Sec. II B results in a M₂⁺(3P_u) formation rate of ~1.5 \times 10^7 / \text{sec}. The effective radiative loss rate per Li⁺ is about 0.1 \Gamma_{\text{Natural}} or 3 \times 10^6 / \text{sec since about 10\% of the Li⁺ is the LiXe⁺ form from which the radiation escapes. The 3P_u formation rate would thus be faster than radiative losses, but at high enough electron densities to yield a Li⁺ quenching rate Q >> R_f the steady-state Li⁺ and LiXe⁺ densities are still determined simply by the effective electron temperature. Since the LiXe⁺ formation rate is
very much faster than the Li$_2$(a$^3\Pi_u$) rate, $R_f$, one could still obtain
efficient pulsed operation if the stimulated emission rate for LiXe$^*$
exceeded $R_f$. In essence, each excited Li$^*$ would branch to Li$_2^*$(a$^3\Pi_u$)
or a LiXe$^*$ stimulated photon in the ratio of $R_f$ to the stimulated
emission rate.

Thus the LiXe laser system might operate efficiently in the 910–930 nm
region in spite of the effects of Li$_2$, which were not considered in Ref. 2.
V. CONCLUSION

The alkali dimer A-X band appears to be a promising molecular laser system which could provide a high efficiency, high energy-density laser gain or oscillator medium in the 0.7-1.2 μm wavelength region. For the pulsed, high buffer-gas pressure system a stored laser energy density of \( \sim 2 \text{ J/λ} \), of which \( \sim 1/7 \) is immediately available, is postulated in the text. This \( \sim 2 \text{ J/λ} \) energy density can be delivered once per \( M_2^* \) relaxation time, which is \( \sim 5 \text{ nsec} \) at an electron density of \( 10^{15} / \text{cm}^3 \), and a single pulse might last more than \( 10^3 \) relaxation times before loss of net gain occurs due to gas heating. This stored energy could be increased by a factor of \( \sim 10 \) if the effective electron temperature were increased to 2 eV from the value of 0.5 eV used to demonstrate the threshold condition in the Na case. At these higher electron temperatures, higher alkali densities can also be entertained, yielding still greater energy densities. Based on discussions in Sec. II E, energy conversion efficiency in excess of 50% may also be possible.

The principal deficiency of this system is a consequence of the fact that the \( A_2^{1+} \) radiating state is not the lowest state of the first excited configuration. The lower \( a_2^3 \Pi_u \) state provides an unfortunate non-radiative channel for loss of excitation energy, as well as a reservoir for excitation energy. This \( a_2^3 \Pi_u \) stored energy may be largely convertible into laser energy, but only at a rate governed by \( a_2^3 \Pi_u \rightarrow A_2^{1+} \) collisional mixing. In addition, if the \( a_2^3 \Pi_u \) state predissociates or dissociates rapidly due to X collisions efficient energy conversion will not be possible and even net gain may not be feasible.

The type of laser studied here is a prototype for which there are doubtless many possible candidates. The key element of displaced
potentials between the ground and a low-lying excited state of a molecule is quite common and has been utilized in other laser systems. The two-step excitation method considered here, atomic excitation followed by "excimer formation," can be applied when the ground-state binding leads to a small fraction $[M_2]/[M]$. A direct $M_2 + M_2^*$ excitation can be used when $[M_2]/[M]$ exceeds 1. In both cases the buffer gas provides the necessary heat sink that maintains the near-thermal distribution of $M_2$ population that is necessary to preserve net gain and efficiency. Numerous candidates span the ultraviolet to infrared wavelength range. Unfortunately, spectroscopic data and potentials do not exist for very many of the diatomic molecules one would like to consider, much less for the polyatomics. This is perhaps a principal reason why $H_2$ is the first gas laser based on this principle of separated absorption and emission wavelength regions. It is also a principal reason why this report is restricted to alkali dimers, the most thoroughly studied of the metal-dimer molecules. There are almost certainly better molecules for this purpose; we have been able to investigate only these few whose optical properties are fairly well known and even here our conclusions are very uncertain due to lack of information on the $a^3\Pi_u$ and $x^3\Sigma_u$ nonradiating states. We hope this report will indicate some of the needs for basic molecular data.
Appendix A: Predissociation

If the $a^3\Pi_u$ state intersects the $x^3\Sigma_u^+$ state in an attractive region of the $a^3\Pi_u$ state, predissociation will rapidly deplete the excited state population. We are aware of only one potential calculation and one experiment which bear on this question. The $Na_2$ triplet potentials calculated by Bertoncini and Wahl$^9$ are reproduced in Fig. 2a, where it can be seen that they do not cross. These $x^3\Sigma_u^+$ and $a^3\Pi_u$ states are separated by 0.15 eV at the radius where $a^3\Pi_u$ becomes repulsive and more at larger separations, so predissociation for bound $a^3\Pi_u$ states or thermal $Na^+ + Na$ collisions should be highly forbidden. The accuracy of these potentials are estimated to be on the order of 0.1 eV, so this is encouraging evidence against predissociation as a major loss mechanism in the $Na_2$ case. Even if a crossing occurred where $a^3\Pi_u$ is weakly attractive, only weakly bound $a^3\Pi_u$ state molecules would rapidly predissociate. Some recombination measurements$^{27}$ and calculations$^{28}$ indicate that most recombination is into strongly bound states, but others indicate binding by only a few kT. In the former case predissociation of only weakly bound states would not be a serious loss mechanism, and vice versa.

Kempter et al.$^{30}$ have measured the collisional excitation of the K resonance line due to K – K collisions. This process can be attributed to an electronic transition from the $x^3\Sigma_u$ to $a^3\Pi_u$ state at or near the crossing point. They interpret their data (Fig. 2 of Ref. 30) as indicating a threshold at 1.6 eV corresponding to the K resonance-line energy, but in fact the reported excitation was observed far below 1.6 eV. This sub-threshold excitation is tentatively attributed by Kempter et al. to a $K_2$ component in the velocity-selected beam. If the sub-threshold excitation is extrapolated above threshold and subtracted from the total
observed excitation, the residual K + K portion appears to have a very gradual onset from 1.8-2.4 eV followed by a rapid rise above ~2.4 eV. The relative Doppler spread is \( 2\sqrt{\frac{E_{cm}}{kT}} \approx 0.6 \text{ eV} \) for \( E_{center} \) of mass = 2 eV and a target temperature of \( T \approx 600^\circ \text{K} \), so the gradual onset below 2.4 eV is consistent with a threshold at ~2.4 eV due to an \( \chi_3^3_{\Sigma_u} - \alpha_3^3_{\Pi_u} \) crossing at this energy. The \( \alpha_3^3_{\Pi_u} \) state would then be ~0.8 eV repulsive at the crossing, ruling out rapid predissociation. As for the Na\(_2\) case this is a somewhat uncertain conclusion, but it appears fairly certain that K\(_2\) and Na\(_2\) molecules that are formed or collisionally relaxed into strongly bound states probably will not predissociate.
Appendix B: The Excimer Formation and Quenching Rate Constants

We will estimate the excimer recombination rate constant $k_f$ for $M^* + M + X + M_2^* + X$, then discuss the quenching rate constant $k_q$ for $M_2^*(A^1\Sigma_u^+ + a^3\Pi_u^-) + X + M_2(x^3\Sigma_u^-) + X$ for the Na and Xe case at $T \approx 810^\circ K$.

This recombination is quite different from any specie whose recombination has been studied to date. For example, the Na$_2^* A^1\Sigma_u^+$ state has $R_e \approx 4 \text{ \AA}$, a very long range ($R^{-3}$) attraction, and about 1 eV of binding and the $a^3\Pi_u$ state is supposed to have a similar $R_e$ and long-range attraction with somewhat greater binding. By comparison, the H$_2$ and halogen systems that have been most extensively studied have $R_e \approx 1$ and 2 \AA respectively, comparatively minor long range forces, and $\sim 5$ and 2 eV binding, respectively. The RbXe* and NaXe* recombinations studied in our laboratory have $R_e \sim 3.5 \text{ \AA}$, moderately long-range attraction, but typically only 0.1 eV of binding. We will use known $k_f$ for these systems and rough scaling arguments based on comparisons of pair interactions to guess at the $k_f$ of interest here. We will consider the recombination as a binary collision with either of a pair of atoms that are within the necessary proximity of each other for binding. Thus we will scale the recombination rate constant as a binary collision rate constant times pair interaction volume. In addition to these direct formation rates, the process $MX^* + M + M_2^* + X$ can contribute and will be estimated.

The H + H + Xe + H$_2$ + Xe recombination rate constant is about $8 \times 10^{-33}$ cm$^6$/sec at 300$^\circ$K and it apparently follows a temperature dependence that would yield about $3 \times 10^{-33}$ cm$^5$/sec at $\sim 3000^\circ$K, corresponding to the same $D_e/kT$ as Na$_2^*(A^1\Sigma_u^+)$. Since the separation at which Na$_2^*$ is attractive by kT is about 6 times that of H$_2$, one might expect a factor of $6^3$ increase due to this. The Na-Xe and Na*-Xe
interactions also have ~5 times the range of H-Xe, but H$_2$-Xe velocities are ~4 times greater than Na$_2^*$-Xe, so a net increase of ~6 might be expected due to these factors. The statistical branching of Na + Na$^*$ into Na$_2^*$($A^1\Sigma_u^+ + a^3\Pi_u$) is about 1/3 versus 1/4 for H + H $\rightarrow$ H$_2$($A^1\Sigma$). In addition, some of the Na$_2$ formed in the $b^3\Sigma_g^+$ and $b^1\Pi_u$ states will be transferred to the $a^3\Pi_u$ and $A^1\Sigma_u^+$ states by X collisions. Thus from these considerations we might infer $k_f \approx 10^{-29}$ cm$^6$/sec for Na$_2^*$(A$^1\Sigma_u^+ + a^3\Pi_u$).

The Br + Br + Xe $\rightarrow$ Br$_2$ + Xe recombination rate constant is about $2 \times 10^{-32}$ cm$^6$/sec at $\beta D_e$ comparable to those of interest here. In this case, the Na$_2^*$(A) range for $\sim$kT attraction is ~3 times that for Br$_2$, the Na-Xe and Na$^*$-Xe interactions are somewhat of longer range than BrXe, the statistical branching is about 6 times more favorable for Na$_2$(A$^1\Sigma_u^+ + a^3\Pi_u$), and the velocities are comparable. Thus $k_f \sim 7 \times 10^{-30}$ cm$^6$/sec might be inferred from this.

The Rb$^*$ + Xe + Xe $\rightarrow$ RbXe$^*$ + Xe recombination rate constant is $8 \times 10^{-32}$ cm$^6$/sec at $\beta D_e \approx 3$. In this case, the Na$_2^*$ interaction is kT attractive at about 2 times the RbXe$^*$ range and the stabilization via Rb$^*$-Xe is similar to Na$^*$-Xe. The statistical branching is a factor of two more favorable for RbXe$^*$($A^2\Pi$) than for Na$_2^*$(A$^1\Sigma_u^+ + a^3\Pi_u$), but this is compensated by velocity differences. The effects of the greatly increased $\beta D_e$ of Na$_2^*$ are very uncertain. The situation is badly confused, since H$_2$ and Br$_2$ recombination show rather weak temperature dependence ($\sim T^{-0.4}$), whereas the RbXe$^*$ recombination measurements indicated a rapid increase per state [$\sim \exp(0.38E_B)$] with the binding energy $E_B$ of the state. Thus the former implies an increase of only a factor of 2 ($\beta D_e \approx 20$ for Na$_2^*$ compared to 3 for RbXe$^*$), whereas the latter indicates about $\exp 4 \approx 50$. The weak temperature dependence may be indicative of changes at large $\beta D_e$. 

values and vice versa so that the arithmetic mean might be taken as a first guess. This would yield \( k_f \approx 5 \times 10^{-30} \) cm\(^6\)/sec with a very large uncertainty.

All states of NaXe\(^*\) will be in equilibrium with the gas temperature at \([Xe] \approx 10^{19}/\text{cm}^3\). From recent spectroscopy,\(^{24}\) the NaXe A-state potential is known and yield from Eq. (1) an equilibrium constant of about \( 10^{-21} \) cm\(^3\) at 810 K ([NaXe\(^*\)] \approx 10^{-21} \) cm\(^3\) [Na\(^*\)][Xe]). The concentration of quasi-bound NaXe\(^*\) states, which can also contribute to NaXe\(^*\) + Na \rightarrow Na_2\(^*\) + Xe via the energy transfer mechanism, are comparable. The rate \( R_S \) for NaXe\(^*\) + Na \rightarrow Na_2\(^*\) + Xe should be dominated by the long-range Na_2\(^*\) interaction which is \( \sim kT \) attractive at \( R_T \approx 8 \) Å. Direct statistical branching to \( \Delta A \Sigma_u^+ + \Delta a \Pi_u \) is 1/3, and is enhanced by cascading from \( \Delta B \Pi_u \) and \( \Delta b \Sigma_g \). Thus,

\[
R_S \approx \frac{R_T^2}{2} \approx 8 \times 10^{-10} \text{ cm}^3/\text{sec}
\]

and \( R_f \approx 1.6 \times 10^{-30} \) cm\(^6\)/sec for this process. This rate should be added to the direct rate estimated above.

Thus a variety of arguments, although very approximate, lead to an effective \( k_f \approx 8 \times 10^{-30} \) cm\(^6\)/sec for the sodium case. The \( \beta_0 \) and range of the Na A-state are about the same as for Na_2 and this is probably indicative of the \( \Delta a \Pi_u \) state as well, so we can expect an equivalent rate for Na_2\(^*\) recombination. For Rb_2\(^*\) and Cs_2\(^*\), the A-states are shallower, but radiative lifetimes should be longer due to increasing wavelength, temperatures are lower, and interaction distances should increase. Thus, the ratio of \( R_f \) to \( \Gamma \) for Na is probably typical of the heavier alkalis as well. For \([M_2] = 10^{17}/\text{cm}^3\), \([X] = 2 \times 10^{20}/\text{cm}^3\), and \( k_f = 8 \times 10^{-30} \) cm\(^6\)/sec \( R_f = 1.6 \times 10^8/\text{sec} \), as indicated in Fig. 7.

Quenching of the \( M_2\(^*\) \Delta a \Pi_u \) state to the \( \Delta x \Sigma_u \) state by collision with a rare gas atom depends on the form of the interacting surfaces. If the Xe + \( x_2 \Sigma_u \) adiabatic potential surface crossed the Xe + \( a \Pi_u \) surface in a
thermally accessible region, the cross section would be almost of gas-kinetic magnitude and $R_q$ in Fig. 7 would be about $100 \times 10^8$ sec. As in the case of predissociation, this would preclude efficient laser operation, but here we are aware of no relevant information. If the $\text{Xe} + M_2 (x^3 \Sigma_u)$ and $\text{Xe} + M_2 (a^3 \Pi_u)$ surfaces do not approach more closely than $\sim 0.3$ eV, the quenching is highly improbable due to the necessity of transferring a great deal of kinetic energy to the M atoms. Such transfer is difficult in slow neutral collisions due to the adiabaticity criteria, with the transition probability becoming exponentially small in the Massey parameter $(\Delta E/h)^{\tau_{\text{collision}}}$. Such very small rare gas quenching cross sections have been observed between CO and OH states of the same multiplicity, as here, but with larger energy spacings.\textsuperscript{32} Thus, just as with predissociation, our expectation is that this quenching will be either a dominant loss mechanism or a negligible one, depending probably on the particular rare gas and alkali used. Only the slow loss case is of interest in studying possible laser operating conditions, so this is adopted in Fig. 7b and Table II.

Acknowledgments

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