HIGH PRESSURE NOBLE GAS ALKALI VAPOR MIXTURES AND THEIR VISIBLE--ETC(U)
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HIGH PRESSURE NOBLE GAS ALKALI VAPOR MIXTURES
AND THEIR VISIBLE AND INFRARED EXCIMER BANDS.

FINAL REPORT

Prepared by

William Mopper
Professor of Physics

Feb 1980

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P.O. Box 12211
Research Triangle Park, NC 27709

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Columbia Radiation Laboratory
Columbia University
538 West 120th Street
New York, New York 10027

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**Authors:** Professor William Happer

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**Abstract:**

The infrared absorption of saturated alkali vapors has been measured for the first time. New absorption bands are tentatively assigned to triplet dimer molecules and also to trimer molecules.
FOREWORD

During the period November 15, 1976 through November 14, 1979 we have carried out fundamental studies of the optical properties of dense alkali vapors in the visible and near infrared region of the spectrum. The most important result of this work has been our discovery of a new region of infrared absorption between 1μ and 2μ in the saturated vapors of sodium, potassium, rubidium and cesium. This new region of absorption appears to be due to the transition $^3\Sigma_u \rightarrow ^3\Sigma_g$ of the alkali dimer molecule, a transition which has never been identified before in alkali vapors but which is responsible for the intense ultraviolet emission continuum of a hydrogen discharge lamp. Should the same emission continuum exist for the alkali vapors, as we suspect from the results of our work on absorption, the alkali vapors could serve as media for very efficient, tunable excimer lasers in the spectral region between 1μ and 2μ. A more pessimistic interpretation of the data is that the absorption is due to trimers. If so the prospects for laser action are less promising. Further work is being done to unambiguously establish the nature of the newly discovered absorption bands.
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REPORT OF PROGRESS

Alkali vapors have long been of interest because of the high efficiency with which they convert electrical power into visible and near infrared light. For example, high pressure sodium lamps are the most efficient industrial source of visible light now available. In spite of their utility as sources of incoherent light, alkali vapors have proven to be somewhat disappointing as laser media. While both alkali atoms and alkali diatomic molecules have been made to lase, the efficiencies have been modest and the spectral regions of lasing are already covered by more efficient and convenient lasers.

The main goal of the work supported by Grant DAAG29-77-G-0015 has been to investigate the potential of alkali vapors as laser media in a spectral region 1\(\mu\) to 2\(\mu\) where high power tunable lasers do not yet exist.

For many years alkali vapors were presumed to be transparent in the infrared region of the spectrum beyond about 1\(\mu\) where the strong A band \((X^1\Sigma_g^- \rightarrow A^1\Sigma_u^+)\) terminates. More recently, small amounts of absorption have been discovered just beyond the edge of the A band. This absorption has been assigned to the weak intercombination band \((X^1\Sigma_g^- \rightarrow a^3\Pi_u^-)\) and it is particularly noticeable for the heavier alkali elements rubidium and cesium for which L and S are rather poor quantum numbers.

Two years ago we discovered that all alkali vapors have a previously unknown absorption band which extends well beyond the edge of the A band and the intercombination bands. By examining the temperature dependence of these absorption bands we have shown that a very plausible assignment of the new absorption is the transition \((^3\Pi_u \rightarrow ^3\Pi_g)\) between the lowest triplet sigma states of the alkali dimer molecule. The transition is very
important in a hydrogen discharge where it gives rise to the intense ultraviolet continuum radiation which is often used as a light source in spectroscopy. The absence of an analogous emission continuum in alkali vapors has long been a puzzle. Should the newly discovered absorption bands indeed turn out to be the \( ^3\Sigma_u \rightarrow ^3\Sigma_g \) transition, this troublesome problem will finally be laid to rest. A more detailed account of our first studies of this new transition is contained in Appendix A.

In a recent theoretical paper, Konovalov and Julienne have shown that the \( ^3\Sigma_g \rightarrow ^3\Sigma_u \) transition would make an excellent excimer laser in the near infrared region of the spectrum. They estimate that stimulated emission cross sections for the transition are as large as \( 10^2 \), a value which is comparable to that for the well known rare-gas-halide excimer lasers.

While experimental and theoretical work on the significance of the \( ^3\Sigma_u \rightarrow ^3\Sigma_g \) transition is encouraging, there are still unsettled questions about the nature of the absorption. For example, it seems certain that trimers are responsible for some of the absorption and it is conceivable that trimers could account for the bands we have assigned to the transition \( ^3\Sigma_u \rightarrow ^3\Sigma_g \). Should this prove to be true the outlook for laser action would be poor indeed because the trimer bands would represent a severe parasitic loss mechanism. Further work is planned to unambiguously identify the nature of the infrared absorption.

The new region of absorption was discovered accidentally while we were investigating the properties of an interesting cross fluorescent emission band in the infrared spectrum of the cesium molecule. A description of this work, which is the first published example of cross fluorescent emission bands in alkali dimer molecules, is contained in Appendix B.
Another interesting result of our work during the period of this grant was the discovery of visible emission bands from potassium polyxenide molecules. This peculiar molecule, $K^{+}Xe_{n}$, with $n = 1, 2, 3, 4 \ldots$, seems to consist of a cluster ion $K^{+}Xe_{n}$ to which an electron is bound in an orbit resembling that of the first excited atomic $S$ state. When the potassium polyxenide molecule decays with the emission of intense green fluorescence, the ground-state molecule dissociates. A more detailed description of the work on potassium polyxenide molecules is contained in Appendix C.
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PUBLICATIONS
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New Infrared Absorption Bands of Alkali Vapors

N. D. Bhaskar, E. Zouboulis, T. McClelland, and W. Happer

Columbia Radiation Laboratory, Department of Physics, Columbia University, New York, New York 10027
(Received 26 December 1978)

We have identified two new infrared absorption bands in potassium vapor. The band between 1.1 and 1.6 \( \mu \)m is attributed to the \( K\) \( (^3\Sigma_u^+ \rightarrow ^1\Sigma_u^+)\) transition, the absorption analog of the intense emission continuum of \( K\). The absorption at wavelengths longer than 1.6 \( \mu \)m is probably due to trimers.

In this paper we report on a new region of absorption of infrared radiation by alkali-metal vapors. Recently, Chertoprud\(^1\) has reported that absorption exists in saturated potassium vapor at wavelengths well beyond the edge of the \( A\) band (1.1 \( \mu \)m), and the absorption extends at least as far as 2.5 \( \mu \)m. Chertoprud\(^1\) assigns this absorption to the intercombination transition \( (\Lambda \Sigma_u^+ \rightarrow \Sigma_u^-)\). Our recent experiments confirm that absorption does exist in the alkali vapors potassium, rubidium, and cesium at wavelengths at least as long as 2.5 \( \mu \)m. However, our observations differ considerably from those of Chertoprud\(^1\) since we find at least two distinct absorption bands, a much smaller attenuation coefficient at low temperatures, a complex dependence on wavelength, and a temperature dependence which unambiguously rules out the assignment of...
this absorption to the transition \( \lambda_{1}^{\text{min}} - \lambda_{2}^{\text{max}} \). As we shall show below, the most likely assignment of this absorption \( 1.1-1.6 \mu m \) is the previously unobserved transition \( \lambda_{1}^{\text{min}} - \lambda_{2}^{\text{max}} \) in the alkali dimers. This is the analog of the powerful infrared emission continuum of \( \text{H}_2 \) molecules, a transition whose apparent absence in the emission spectrum of alkali dimers has long been a puzzle. The longer-wavelength absorption \( 1.6-2.0 \mu m \) cannot be assigned to dimers, and it seems consistent with electronic absorption bands in clusters of three potassium atoms or trimers. These new absorption bands lie in a broad spectral region which was previously considered to be transparent and they add a new and important element to considerations of alkali-metal vapors for laser media or heat-transfer media.

The experimental apparatus used in our work is shown in Fig. 1. The effective length \( z \) (about 20 cm) of the vapor column in a heat-pipe oven is determined from the measured outside temperature profile and the length of the heat pipe. The uncertainty in \( z \) is about 5%. The saturated vapor pressure of the alkali metal is controlled with an inert buffer gas of argon, neon, or helium. At pressures above 300-Torr neon and argon are found to produce dense clouds of alkali-metal fog. We found helium to be free of this problem, presumably because of the high kinematic viscosity and heat conductivity of the helium. Our measurements of vapor pressure \( P \) and temperature \( T \) for potassium were consistent to within about 1% with the accepted empirical formula:

\[
\log_{10} P_{\text{sat}} = -7.18 + (4435/T). 
\]

The Clausius-Clapeyron equation (1) implies that \( T \), the latent heat of vaporization of potassium, is 20.3 kcal mole.

The experimental procedure is as follows. \( I(\lambda, T) \), the intensity of light of wavelength \( \lambda \) transmitted through the vapor at temperature \( T \) and \( I(\lambda, T) \) the transmitted intensity at room temperature \( T_{0} \) are measured, the latter measured at the beginning and end of each run. For a vapor column of length \( z \), the attenuation coefficient \( \alpha(\lambda, T) \) is given by

\[
\alpha(\lambda, T) = \frac{1}{z} \ln \left[ \frac{I(\lambda, T)}{I(\lambda, T_{0})} \right].
\]

Representative data for \( \ln(\alpha, T) \) are plotted as a function of \( T \) in Fig. 1. Note that the data can be fitted very well with a straight line in the temperature interval covered by our experiments. Thus, we may represent \( \alpha \) by the empirical formula

\[
\alpha(\lambda, T) = \exp[A(\lambda) - E(\lambda)/RT].
\]

A summary of our experimental data is shown in Fig. 2 where the measured attenuation coefficient \( \alpha(\lambda, T) \) and the activation energy \( E(\lambda) \) are plotted as a function of \( \lambda \) for \( T = 943 \text{K} \).

In the temperature range involved in our experiments the potassium vapor consists predominantly of free potassium atoms. Bound dimers \( K_{2} \) also exist at about 6\% of the monomer concentration at 943 K. In addition to the bound dimers, unbound pairs of potassium atoms are present at concentrations large enough to cause substantial optical absorption. Trimmers and higher polymers of potassium are also important at the relatively high vapor pressures of our experiments. The attenuation coefficient of the potassium vapor will therefore consist of contributions from various clusters of \( n \) potassium atoms, each of which will contribute a term

\[
\alpha(\lambda, T) = \alpha(\lambda, T)_{\text{total}} = \exp[-V(\lambda)/RT]
\]

to the total attenuation coefficient of the vapor. Here \( V(\lambda) \) is the potential energy of association.

---

**FIG. 1.** Typical data for attenuation of infrared radiation by saturated potassium vapor. The straight lines are the best straight-line fits consistent with the standard deviation of the slope and the standard deviation of the intercept of the straight-line fit. The straight lines were fitted by a least-squares error analysis.
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FIG. 2. Activation energies (points) and attenuation coefficient (solid line) for saturated potassium vapor as a function of wavelength. Error estimates are obtained from least-squares fits to experimental data like that in Fig. 1(b). The error estimates for the absorption coefficient are also shown. Monochromator resolution is 50 Å (full width at half-maximum). Bands I, II, and III are indicated at the bottom of the figure.

of \( n \) potassium atoms into a configuration for which an electronic transition of wavelength \( \lambda \) is possible, and \( R \) is the gas constant. The factor \( b(\lambda) \) includes oscillator strengths and phase-space factors, and \( N_K \) is the number density of potassium atoms. In the case of potassium dimers (4) can be written in the well known form

\[
\sigma_a(\lambda, T) = 2\pi^2 r_c^2 (\lambda / 4 \pi^2)^{2/3} dV [N_K^2 \exp(-V(\lambda)/RT)]
\]

where \( r_c \) is the classical electron radius, \( c \) is the speed of light, \( f \) is the oscillator strength of the electronic transition, \( g \) is the statistical weight of the lower electronic potential curve, and \( \nu = c / \lambda \) is the frequency of a photon which can resonantly excite the molecule between two electronic states at an internuclear separation \( r \).

Saturated potassium vapor consists predominantly of free potassium atoms, and we may therefore approximate the vapor pressure with the partial pressure of the free atoms. Using

\[
\ln\left(\frac{N_K}{N_0}\right) = \ln P - \ln(R T) - (\epsilon - \nu) R T - 1,
\]

where the latent internal energy of vaporization \( \epsilon \) is related to the latent heat \( l \) by \( \epsilon = l - RT_0 \).

\( P_0 \) is a constant, \( P_0 \) is Avagadro's number, and \( T_0 = 943^\circ K \) is a representative temperature which characterizes the conditions of our experiments. Thus, Eq. (4) can be written as

\[
\sigma_a(\lambda, T) = f_0(\lambda) \exp(-\nu(\lambda)/R T),
\]

Comparing (7) with (3) we conclude that the activation energy \( E(\lambda) \) is equal to the sum of the association energy \( V \) and \( \nu \) factors of the vaporization energy \( \epsilon \),

\[
E(\lambda) = \nu(\lambda) = \nu + \nu.
\]

For reference we have indicated the energies \( 2\epsilon = 36.8 \) and \( 3\epsilon = 55.2 \) kcal/mole in Fig. 2.

Three distinct regions of absorption, designated as regions I, II, and III, are indicated in Fig. 2. In band I (\( \lambda = 1.1 \mu \)) the absorption coefficient has values in excess of \( 1 \) cm\(^{-1} \) and activa-
tion energies of ~25 kcal/mole. Band I is the red edge of the well known A band, the strongest absorption band of K dimers. The association energy of the K_K^+ molecule corresponds approximately to the dissociation energy of the K_2K^+ ground-state molecule. The potential energy curves for K_2 are shown in Fig. 3.

Band II (3.14 to 3.6 μm) is a new absorption band which is considerably weaker than the A band and which has a considerably higher activation energy. The activation energy of band II is of the order of 40 kcal/mole while the vaporization energy 2σ of two potassium atoms is 36.8 kcal/mole. The difference, 3.5 kcal/mole, can be interpreted as a repulsive interaction potential between a pair of ground-state K atoms on the K_2 potential curve. Theoretical calculations\(^5\) for Li_2 suggest that the transition (α_2 → α_4) gives rise to a band to the red of the corresponding A band. The band should have a satellite, corresponding to the distance of closest approach of the potential curves (see Fig. 3) at a wavelength which is somewhat greater than twice the wavelength of the first resonance line of the free K atom (7665-7699 Å for K). It is reasonable to identify the observed knee at 1.58 μm in Fig. 3 with the predicted satellite.

The observed magnitude of the attenuation coefficient of band II is also consistent with the value expected for the transition (α_2 → α_4). Using Eq. (5), and substituting therein the following reasonable values for T, T = 3, r = 1 Å, dν = 5 × 10^(-2) sec^(-1) cm^(-1), and V = E(1.2 μm) = 2σ = 37.5 - 36.8 = 0.7 kcal/mole, we find (2.0 μm, 943 K) = 0.6 per meter in satisfactory agreement with the measured attenuation coefficient of 0.3 cm^(-1) from Fig. 2.

In summary, the observed wavelength, activation energy, absorption-coefficient magnitude, and satellite on band II all support the assignment of this band to the transition (α_2 → α_4).

Band III (5.1 to 6 μm) is about a factor of 70 weaker than Band II and it has a substantially higher activation energy (K = 56 kcal/mole). If we attempt to assign band III to a dimer transition we must interpret the high activation energy, E(1.8 μm) = 39.2 kcal/mole, as a repulsive potential energy of 39.2 kcal/mole. For example, one might interpret Band III to the transition of electronic excited II state to α_4. However, the measured magnitude of the attenuation coefficient in band III is about 300 times too big to be consistent with its absorption and any reasonable values of parameters in (5).

It is interesting to note that the activation energy of band III, 56 kcal/mole, is very close to the energy of vaporization of three potassium atoms 3 × 55.2 kcal/mole. Thus, loosely bound alkali trimers are a possible source of the absorption in band III. The number density of oscillator electrons involved in the absorption band is related to the strength, S/σ, of that band by the well known formula \(c = S σ/γ\). For band III (integrated from 1.6-2.0 μm) we estimate \(c\) to be about 5.6 × 10^12 cm^(-2). The total number density of valence electrons in the vapor is very nearly equal to the potassium-atom number density \(N_κ\). The fraction of valence electrons involved in band III is therefore 1.9 × 10^(-4). This is a crude estimate of the ratio of trimers (associated with band III to monomers. Since the trimer association energy is comparable to RT (see Fig. 2), the trimer number density is related to the monomer number density by \(N_κ = c/3 \). For band III we find \(c\) to be 7.8 Å. In view of the known range of interatomic potentials between alkali atoms this is an entirely reasonable value for the characteristic separation of potassium atoms in a loosely bound trimer. We should also point out that the closely analogous trimer H is known from theoretical calculations\(^5\) to have low-lying electronic potential surfaces between which fully allowed electronic transitions are possible; for example, the \(α_2\) and \(α_4\) states of D symmetry. Note that the shorter-wavelength trimer absorption spectrum is completely masked by the powerful dimer absorption bands below 1.6 μm. We are therefore unable to draw any conclusions about the population of trimers (perhaps the great majority\(^5\)) with absorption bands below 1.6 μm.

We have observed analogous absorption bands in rubidium and cesium vapors, and similar experiments for sodium and lithium vapors are also underway. A more extensive paper describing our experimental results for all of the alkali vapors is in preparation.

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LASER-EXCITED CROSS FLUORESCENT EMISSION FROM CESIUM MOLECULES

N.D. BHASKAR, E. ZOUBOULIS, R. NOVAK and W. HAPPER
Columbia Radiation Laboratory, Department of Physics, Columbia University,
New York, New York 10027, USA

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We report the first observation of cross fluorescent infrared emission bands from laser-excited alkali molecules. One example, a newly observed band of Cs₂ between 1.50 and 1.63 μ, is discussed in some detail. These new decay modes allow quantitative experimental studies of low-lying and previously unobserved states of gerade symmetry in alkali dimers.

In this paper we report on our recent observations of a new type of infrared emission band from laser excited alkali molecules. These bands are due to cross fluorescent transitions from the higher excited states of alkali dimer molecules to lower lying and previously unobserved excited states of gerade symmetry. To our knowledge, this is the first observation of cross fluorescent decay modes in alkali molecules.

We were led to search for cross fluorescent emission bands of alkali dimers by the following arguments. The electronic potential curves of alkali dimers are closely correlated with the electronic states of free alkali atoms [1]. The higher excited states of alkali atoms, for example, the 7P, 7S and 5D states of the cesium atom, do not decay predominantly or entirely to lower lying excited states and not to the ground state. The corresponding emission lines lie in the infrared region of the spectrum at wavelengths beyond 1 μ. It is reasonable to look for infrared molecular emission bands corresponding to the infrared atomic emission lines, and, as we shall show below, such bands do indeed exist.

A sketch of our apparatus is shown in fig. 1a. The cell is made of Corning 1720 aluminosilicate glass tubing of inner diameter 21 mm. After baking the cell in a...
vacuum of $10^{-6}$ Torr at 650°C for 10 h, a little (99% pure) cesium is distilled into it before seal off. The cell is seated inside a transparent oven and heated to 350°C. The beam of an argon-ion laser (Spectra-Physics model 165-03) is focused into the cell and one of the blue-green laser lines is selected for exciting the cesium vapor. The fluorescent radiation emitted at right angles to the incident laser beam is focused on the entrance slit (1 mm wide, 10 mm high) of a spectrometer (GCA/McPherson 0.3 m scanning monochromator). The incident laser beam is chopped at a fixed frequency of 196 Hz. A suitable infrared filter is used to filter out the scattered laser light. It also serves to exclude the second order spectra from the diffraction grating. The dispersed fluorescent spectrum is detected with a dry-ice cooled PbS detector (IR Industries, Inc.). The signal at the chopping frequency is detected with a lock-in amplifier, the output of which is fed into a strip chart recorder.

There is considerable emission in the infrared beyond 1 μ. The infrared emission consists of:

(a) A prominent A-X emission band extending from the cesium resonance D line (≈0.85 μ) to 1.2 μ and showing features similar to those reported by Sorokin et al. [2] in a heat-pipe discharge.

(b) Several strong atomic emission lines are observed 7S(1/2)→6P(1/2) (1.36 μ) and 7S(1/2)→6P(3/2) (1.47 μ). Typically, these lines are much more intense than the molecular emission bands.

(c) On the red wing of the 1.47 μ, 7S→6P atomic line we observe previously unreported infrared emission. Some examples of these new bands which extend from 1.50 μ to 1.62 μ are shown in fig. 2. The band shape depends critically on the wavelength of the laser exciting line, and the fluorescent intensity is proportional to the intensity of the exciting light. The strong laser lines at 4880 Å and 5145 Å were used to generate the spectra shown in fig. 2, but analogous spectra could be generated with the weaker laser lines. Studies of the band shape and intensity as a function of cell temperature showed no evidence of significant collisional effects, and in fact none would be expected for the relatively low atomic number densities [Cs] ≈ $10^{15}$ cm$^{-3}$ and short excited-state lifetimes [3] $\tau$ ≤ 27 ns of the states involved in our work.

The energetics of the excitation and fluorescence are shown in fig. 1b for 4880 Å excitation. The 4880 Å absorption is known [4] to be due to molecules near the bottom of the $X^1\Sigma_g^+$ ground state of Cs$_2$. The upper state, which we denote by $F$ in accordance with traditional nomenclature [1], is poorly known and the 4880 Å line may in fact populate several [3] closely spaced excited states. For clarity we have indicated a single state for $F$ in fig. 1b. Since the ground-state symmetry is $\Omega_g$, the $F$-state symmetry must be $\Omega_0$ or $\Omega_1$. The $F$ state is most likely produced in a vibrationally excited state from whence it can decay into various vibrationally excited or dissociative levels of a final state which we denote by $F$. Again, the final state may actually consist of several electronic potential curves, but for clarity we have drawn only one in fig. 1b. From the known energies of the 4880 Å exciting photons and the band of infrared fluorescent photons we know that the energies of the final vibrational or dissociative molecular levels lie about 600 cm$^{-1}$ below the 6P, 6S dissociation limit. The actual potential curve of the final state $F$ must lie lower by an amount equal to the kinetic energy of the final state molecule. Since the thermal energy $kT$ in our experiments is typically on the order of 400 c.n$^{-1}$ and the ground-state dissociation energy [5] is uncertain by about 80 cm$^{-1}$ we cannot exclude the possibility that some of the final state levels lie above the 6P, 6S dissociation limit and are continuum levels.

The observed energies of the final-state levels strongly suggest that the state (or states) $F$ belongs to the 6P, 6S manifold. Since the final state must have the same inversion symmetry $g$ as the ground state and
since the axial angular momentum can differ by no
more than two units, the state $F$ can only be $0^+_g$, $1^+_g$ or
$2^+_g$. States of this symmetry can arise from the terms
$1^1_2$, $3^1_2$, $1^1_0$ and $3^1_0$ of the 6P, 6S manifold. There
is no reason to expect total spin to be a very good
quantum number in the heavy molecule $CS_2$, and we
use the notation of $I, S$ coupling mainly as a conven-
ient bookkeeping device.

We have been unable to find any published informa-
tion, theoretical or experimental, on the location of
the gerade states of the 6P, 6S manifold of $CS_2$. Ho-
ever, several calculations [6] exist for analogous states
in Li$_2$. If the potential curves for $CS_2$ are similar to the
computed curves for Li$_2$, both the $1^1_2$ and $1^1_0$ can be
expected to have weakly attractive potential curves of
the type, sketched in fig. 1b which would be consist-
tent with our observation.

The pronounced undulatory structure of the emis-
sion bands in fig. 2 is similar to the expected spectrum
for Condon internal diffraction [17]. The long wave-
lengt peak at 1.62 $\mu$ would then be a satellite corre-
sponding to a minimum in the difference potential be-
 tween states $E$ and $F$. The fact that the infrared band
stops beyond 1.62 $\mu$ for both 4880 A and 5145 A exci-
tation even though the overall band shapes are very
different supports the identification of 1.62 $\mu$ as the
wavelength of a satellite or head of heads. The nature of
the peak at 1.505 $\mu$ is less clear. Although one
might be tempted to assign the emission at 1.505 $\mu$ to
emission from a turning point in the potential $E$, the
fact that a peak at 1.505 $\mu$ is also present for 5145 A exci-
tation argues against such an interpretation since
one would expect different vibrational states and hence
different turning points to be produced by different exci-
tation lines. Another possibility is that the peak at
1.505 $\mu$ is a second satellite corresponding to the same
or a different pair of states $E$ and $F$. A detailed assign-
ment of the new infrared bands must await the accu-
mulation of more experimental data.

We have observed very similar infrared emission
bands in Rb$_2$ dimers, excited into the $C$ state by 4880
A and 4765 A lines from the Ar* laser [8]. It is reason-
able to expect analogous infrared emission bands to ex-
ist for other alkali dimers. One implication of these
newly discovered cross fluorescent decay modes is that
excited atoms may be produced by fluorescent decay
into continuum levels of lower-lying states which dis-
sociate into excited and ground state atoms. Cross fluo-
rescence can be as important as predissociation in lead-
ing to excited atoms under collision-free conditions.
Since we have discovered that cross fluorescent infra-
red emission bands exist for the $C$ state of Rb$_2$, one
should certainly reevaluate the earlier suggestion that
the excited atoms produced subsequent to the decay
of the C state are solely due to predissociation [9].

In summary, this paper reports on the first observa-
tions of cross fluorescent decay modes for alkali dim-
ers. This establishes the existence of an important and
previously observed decay channel which should be con-
sidered in future analysis of the kinetics of excited
alkali dimers. Further studies of these new decay
modes will help to elucidate the properties of low lying
and previously unobserved molecular states of gerade
symmetry.

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Visible Emission Bands of KXe Polyatomic Exciplexes

T. Yabuzaki, A. C. Tam, S. M. Curry, and W. Happer
Columbia Radiation Laboratory, Physics Department, Columbia University, New York, New York 10027
(Received 2 March 1978)

Intense green emission bands are observed when potassium vapor in several amagats of xenon is illuminated with the 4067-Å line of a krypton-ion laser. The very pronounced dependence of this green band on temperature and xenon density is consistent with the behavior expected for KXe exciplexes with \( n \) ranging from 1 to at least 4.

Radiative processes in dense gases have received considerable attention in the past few years. One of the motivations for the study of such systems has been the great success of excimer lasers in producing efficient, high-power visible and ultraviolet radiation. At sufficiently high gas pressures, excited atoms often react to form bound electronically excited states of rather improbable molecules (noble-gas fluorides\(^1\) and alkali-noble-gas combinations\(^2\)) which are dissociative in the ground electronic states. These "exciplex" molecules are often good laser species since the ground states self-destruct by dissociation and do not accumulate in sufficient numbers to reabsorb the laser light.

In this Letter we report on our observations of an unusual class of polyatomic exciplexes, KXe\(_n\) (58) molecules, which can be thought of as cluster ions KXe\(_n^+\) with \( n = 1, 2, 3, \ldots \), and a rather extended valence electron in an orbit which resembles the first excited state (5s) of the potassium atom.

We produce these exciplex molecules by exciting a glass cell containing saturated potassium vapor in high-density xenon gas with the 4067-Å line of a krypton-ion laser. This laser line, which has a power of 140 mW, excites the pressure-broadened red wing of the (4044 4047)-Å second resonance line of potassium. The fluorescence from the cell is observed with a monochromator. The entire visible region of the spectrum is dominated by an intense green emission band. The most striking features of this band are illustrated in Fig. 1. The band consists of two parts, a well-defined symmetrical peak centered near 5220 Å, which is known\(^3\) to be an emission band of potassium monoxenide KXe(5s) - KXe(4s), and a broad asymmetric emission band between 5300 and 7000 Å which we attribute to the superposed emission bands of polyatomic exciplexes: KXe(5s) - KXe(4s) with \( n = 2, 3, 4, \ldots \).

We shall henceforth refer to these bands as the monoxenide and polyxenide bands, respectively. This system is particularly convenient for quantitative study since the narrow monoxenide emission peak remains well defined over a broad range of temperature and xenon densities and it can be used as a reference of intensity for the polyxenide band.

From data such as that shown in Fig. 1, several important properties of the polyxenide band can be recognized:

1. The polyxenide band narrows substantially at higher temperatures. The monoxenide band, in contrast, broadens slightly with increasing temperature.

2. The polyxenide band broadens substantially with increasing xenon density. The monoxenide band width is comparatively much less affected by xenon density.

3. The peak of the polyxenide band shifts substantially toward longer wavelengths for decreasing temperature.

FIG. 1. Fluorescence spectra of potassium monoxenide and polyxenide at various cell temperatures and xenon densities (given in amagats). At low xenon density (lower curves), the monoxenide component is dominant. The small peaks observed near 4600 and 5720 Å for KXe in 0.9 amagat are due to alkali dimer fluorescence, since they are also observed in the absence of xenon. At high xenon density, the relative intensity of the red-shifted polyxenide component becomes progressively greater as the temperature is reduced.
The dependence of the polyxenide band on temperature and xenon density can be seen with particular clarity by using the monoxenide band as a reference of intensity. We define the relative intensity $S(A, [Xe], T)$ of the polyxenide band to the monoxenide band by

$$S(A, [Xe], T) = \frac{I(A, [Xe], T) - a I(A, [Xe]_o, T)}{a I(A, [Xe]_o, T)},$$

(1)

where $\lambda_0$ is the wavelength of the peak of the monoxenide band, and the constant $\alpha$ is defined by

$$\frac{I(A, [Xe]_o, T)}{I(5220\,\text{A}, [Xe]_o, T)} = \alpha \text{ for } \lambda = 5220\,\text{A}.$$  

(2)

Here $I(A, [Xe]_o, T)$ is defined as the fluorescence spectrum at low xenon densities, when only the monoxenide spectrum is present. We have found that the polyxenide spectrum is negligible at $[Xe] = 0.9$ amagats, and so we can take $I(A, [Xe]_o, T)$ as the fluorescence spectrum at $[Xe] = 0.9$ amagats.

The relative intensity $S$ at a xenon density of 8.4 amagats is shown in Fig. 2(a). The temperature dependence of the relative intensity was found to be given by

$$S(A, [Xe], T) = \frac{\alpha}{I(5220\,\text{A}, [Xe]_o, T)} \exp \left[ E(A) / kT \right].$$

(3)

Some typical plots of $\ln S(A, [Xe], T)$ versus $1/T$ are shown in Fig. 2(b). The slopes of the straight lines in Fig. 2(b) are proportional to the energies $E(A)$. We have made plots similar to those of Fig. 2 for xenon densities of 11.4, 8.4, 6.6, 6.4, 5.4, and 4.0 amagats. We find that the energies $E(A)$ are independent of the xenon density to within our experimental accuracy of $\pm 5\%$. They can be well represented by the empirical formula

$$E(A) = 2.125A - 10675,$$

(4)

with $E(A)$ in cm$^{-1}$ and $A$ in the range of 5400–6400 A.

Our measurements of xenon density are probably in error by $\pm 10\%$ because of the cell preparation procedure, which consists of freezing xenon at a known initial temperature, pressure, and volume into a small glass cell of known volume. To within the uncertainties of the xenon-density determination, the constants of proportionality $\alpha$ of Eq. (3) have a power-law dependence on the xenon density,

$$\alpha = \frac{1}{n} \exp \left[ -h \frac{\lambda}{kT} \right],$$

(5)

where the exponent $n(\lambda) - 1$ depends strongly on wavelength and can be represented by the empirical formula

$$n(\lambda) = 1.74 \times 10^{-5}\lambda - 8.23$$

(6)

with $\lambda$ in angstroms.

Finally the line shape factor $s(A)$, which is independent of temperature and xenon density over the range of our experimental investigations, $110^\circ \text{C} < T < 300^\circ \text{C}$ and 1 amagat $\cdot [Xe]$, 12 amagats, is given by the empirical formula

$$s(A) = 1778.5 - 0.668A + 6.28 \times 10^{-9} A^2.$$  

(7)

In summary we have found that over a rather large range temperature and xenon density the polyxenide emission band is represented by the formula

$$S(A, [Xe], T) = s(A) \times \exp \left[ -h E(A) / kT \right].$$

(8)

The parameters, $E(A)$, $n(A)$, and $s(A)$ are plotted in Fig. 3.

Because nothing is yet known about the potential surfaces for polyxenide molecules we cannot give a detailed theoretical analysis of the experimental data. However, we can assign a plausible physical meaning to the empirically determined parameters of (8). We may assume that each polyxenide species K$[Xe]_n$ has a characteristic emission band, similar but broader than the
haltrum occurs at we see that All bands of attached n(X). The density dependence of the fluorescence of wave- become KXe. (5S) for density systems we are studying (two-body col- of potassium polyxenide molecules which

The polyxenide bands of Fig. 2 therefore consist of tile superposed and unre- solved emission bands of KXe, KXe,, KXe,, etc. Collisional rates are very fast in the high density systems we are studying (two-body col- lision rate is ~ 10^10 sec^-1, and three-body col- lision rate is ~ 10^10 to 10^11 sec^-1 for a xenon density of 10^3 cm^-3). The radiative decay rate of K(5S) is comparatively slow (2 · 10^-7 sec^-1).

Hence we expect to have thermal equilibrium among the various species K(5S), KXe(5S), and KXe(3S) for n being 2, 3, ..., Therefore we expect the intensity of the emission band due to KXe to be proportional to [Xe]^n. Since there is substantial overlap of these bands the apparent density dependence of the fluorescence of wave- length λ is [Xe]^{n(p)} where n(λ) is the measured noninteger exponent represented by the empirical formula (6). In this interpretation the exponent n(λ) is the average number of xenon atoms at- tached to a potassium atom when the fluorescent wavelength is λ. The values λ, defined by n(λ) = ρ with ρ = 2, 3, 4, etc., can be identified approximately as the peak wavelengths of the emission bands of KXe, KXe,, KXe,, etc. From Fig. 3 we see that λ_p = 5500, λ_3 = 5900, and λ_4 = 6400 Å. The peak of the well-resolved monoxenide spec- trum occurs at λ_p = 5220 Å.

The energy E(λ) can be thought of as the internal energy (not enthalpy because of our conditions of constant density rather than constant pressure) released in the reaction

KXe(5S) + (n - 1)Xe ← KXe,(5S) + E.

We may define a quantity \( B(λ) \) by

\[
B(λ) = E(λ) \left[ n(λ) - 1 \right],
\]

and we shall call \( B(λ) \) the mean binding energy per xenon atom attached to the KXe(5S). This mean binding energy is only approximately equal to the mean energy required to detach a xenon atom from the polyatomic molecule (the two energies differ by a quantity of the order of \( kT \)).

Figure 3 shows a plot of \( B(λ) \), which is of the order of 100 cm^-1 per xenon, and it increases slightly as more xenons are added. In our experiment, the thermal energy \( kT \sim 300 \text{ cm}^{-1} \), and so any given Xe atom in the cluster has a probability of only 0.1 to be moving fast enough to escape from the cluster.

The line-shape factor \( G(λ) \) is perhaps the most remarkable property of the polyxenide band. The function \( G(λ) \) is proportional to a factor which measures the statistical weight of the configurations of potassium polyxenide molecules which radiate at λ, and a mean transition rate of the configurations. Since the statistical weight factor decreases with increasing λ, the rapid growth of \( G(λ) \) with increasing λ must be due to an in- crease in the decay rate with λ. Indeed we expect a substantial increase in the radiative transition rate with λ, that is, with the number of attached xenon atoms, because both the monoxenide and polyxenide emission bands of Fig. 1 correlate with a highly forbidden electronic transition of the free atom K(5S) – K(4S). Each additional xenon atom in KXe(5S) will cause further mixing of the electronic wave functions of the free potassium atom, and the radiative transition will therefore become increasingly more allowed as more xenons are attached. The unprecedented promi- nence of the green potassium polyxenide band is due to the fact that it originates from a forbidden electronic transition of the free potassium atom. This seems to be one of the main reasons that multiple-perturber effects are so much more striking in the data presented in this paper than in the pressure-broadened resonance lines of the alkali atoms. Since the first excited \( J' \) states of free alkali atoms have fully allowed transition rates to the ground state, they can only be weak- ened by multiple-perturber effects, while forbidden lines are strongly enhanced.

The nature of these polyxenide exciplexes is
A sketch to indicate the dimensions of such a system is shown in Fig. 4.

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FIG. 4. Schematic representation of the physical dimensions of potassium polyxenide molecules. The ionic core of K⁺ has a radius of 2.5\text{Å} (\text{Å} = \text{Bohr radius}) and a xenon atom has a radius, 3.6\text{Å}. For the 55 state of potassium the mean radius of the electron charge distribution is 11.8\text{Å}, so that the xenon atoms are primarily affected by the polarizing influence of the ionic core. After a transition to the ground state, the electronic mean radius is only 4.3\text{Å}, and the Xe atoms are no longer bound.

still uncertain, but it is interesting to note that cluster ions of the form K⁺(H₂O)ₙ have been extensively studied, and six or more waters of hydration are observed by mass-spectroscopic techniques. Similar bonding of alkali ions to other neutral molecules (O₂, N₂, and CO₂) has been observed and calculated theoretically. The highly polarizable noble gas xenon (\sigma = 4 \text{Å}) can be expected to form analogous cluster ions K⁺Xeₙ, and an electron could bind to such a cluster ion to form the initial and final states of the polyxenide transitions reported in this paper. A

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[Notes and references omitted for brevity]
Dr. William Happer, Principal Investigator (Columbia University)
Dr. A. Tam (now at IBM Research Laboratories, San José, California)
Dr. S. Curry (now at Texas Electronics, Dallas, Texas)
Dr. T. Yabuzaki (now at Kyoto University, Japan)
Dr. N. D. Bhaskar (Columbia University)
Dr. E. Zouboulis (now at the Institute for Physical Chemistry, Athens, Greece)
Mr. R. Novak (Columbia University)
Mr. A. Vasilakis (Columbia University)
Mr. T. McClelland (Columbia University)