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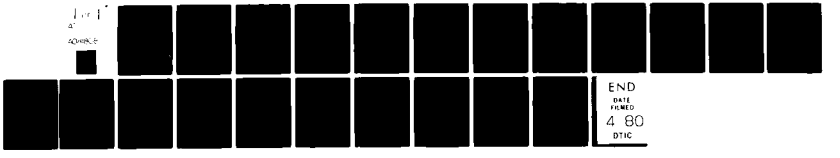

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HIGH PRESSURE NOBLE GAS ALKALI VAPOR MIXTURES AND THEIR VISIBLE AND INFRARED EXCIMER BANDS.

FINAL REPORT

Prepared by

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Professor of Physics

Feb[redacted]80

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(November 15, 1976 - November 14, 1979)

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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.

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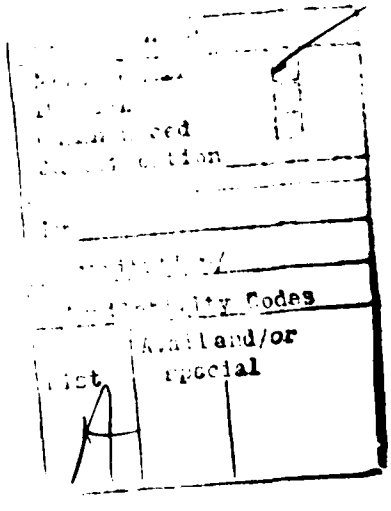
FOREWARD

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 1μ to 2μ 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 1μ where the strong A band ($X^1\Sigma_g \rightarrow A^1\Sigma_u$) terminates. More recently,[1] 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[2] 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 ($^3\Sigma_u \rightarrow {}^3\Sigma_g$) 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[3] 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 10Å^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 $^3\Sigma_g \rightarrow {}^3\Sigma_u$ transition is encouraging, there are still unsettled questions about the nature of the absorption. For example, it seems certain[2] 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[4] 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.[5] This peculiar molecule, KXe_n, with n = 1, 2, 3, 4 . . . , 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 gree 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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APPENDIX A

VOLUME 42, NUMBER 10 PHYSICAL REVIEW LETTERS 5 MARCH 1979

New Infrared Absorption Bands of Alkali Vapors

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(Received 26 December 1978)

We have identified two new infrared absorption bands in potassium vapor. The band between 1.1 and 1.6 μm is attributed to the K_2 ($^3\Sigma_u^+ - {}^3\Sigma_g^+$) transition, the absorption analog of the intense emission continuum of H_2. The absorption at wavelengths longer than 1.6 μm 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 μm), and the absorption extends at least as far as 2.5 μm. Chertoprud[1] assigns this absorption to the intercombination transition ($X^1\Sigma_g^+ - {}^3\Sigma_u^+$). 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 μm. 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 ($X^1\Sigma_g^+ - {}^3\Sigma_u^+$). As we shall show below, the most likely assignment of the shorter-wavelength absorption (1.1–1.6 μm) is the previously unobserved transition (${}^3\Sigma_u^+ - {}^3\Sigma_g^+$) in the alkali dimer molecule. This is the analog of the powerful ultraviolet emission continuum of H_2 molecules, a transition whose apparent absence in the emission spectrum[2] of alkali dimers has long been a puzzle. The longer-wavelength absorption (1.6–2.0 μm) 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 ℓ (about 20 cm) of a vapor column in a heat-pipe oven[3] is determined from the measured outside temperature profile and the length of the heat pipe. The uncertainty in ℓ is about 5%. The saturated vapor pressure of the alkali metal is controlled with an inert buffer gas of argon, neon, or helium. At gas 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[4]

$$\log_{10}P_{mm} = 7.18 - (4435/T). \quad (1)$$

The Clausius-Clapeyron equation (1) implies that l, 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 λ transmitted through the vapor at temperature T and $I(\lambda, T_r)$ the transmitted intensity at room temperature T_r are measured, the latter measured at the beginning and end of each run. For a vapor column of length ℓ, the attenuation coefficient $\alpha(\lambda, T)$ is given by

$$\alpha(\lambda, T) = \ell^{-1}\ln[I(\lambda, T_r)/I(\lambda, T)]. \quad (2)$$

Representative data for $\ln\alpha(\lambda, T)$ are plotted as a function of $1/T$ 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 α by the empirical formula

$$\alpha(\lambda, T) = \exp[A(\lambda) - E(\lambda)/RT]. \quad (3)$$

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 wavelength λ for $T = 943$°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. Trimers 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

$$\alpha_n(\lambda, T) = b_n(\lambda)N^n\exp[-V_n(\lambda)/RT] \quad (4)$$

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

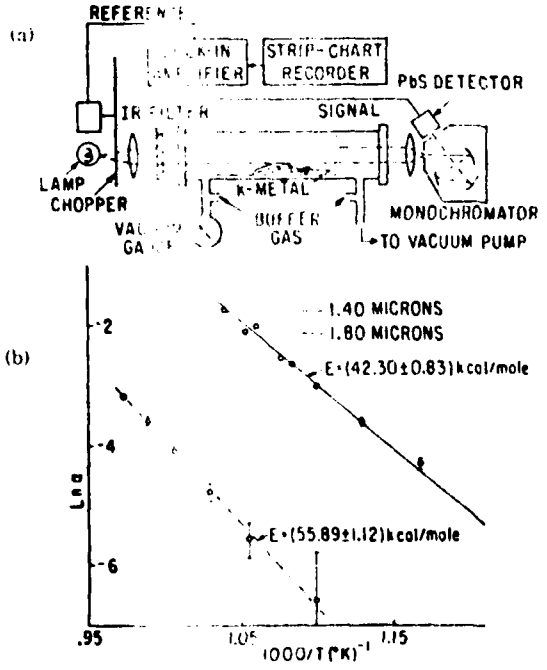

FIG. 1. (a) Apparatus. (b) Typical data for attenuation of infrared radiation by saturated potassium vapor. The straight lines and the standard deviation of the slope were obtained by least-squares error analysis.

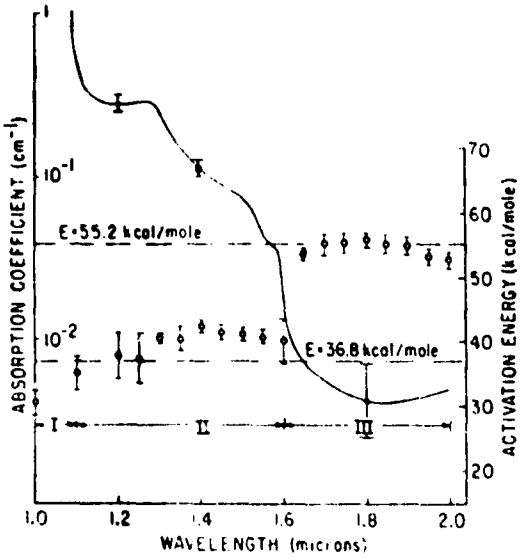

FIG. 2. Activation energies (points) and attenuation coefficient (solid line) for saturated potassium vapor as a function of wavelength. Error estimates are obtained from least-squares fits to experimental data like that in Fig. 1(b). The error estimates for the absorption coefficient are also shown. Monochromator resolution is 50 Å (full width at half-maximum). Bands I, II, and III are indicated at the bottom of the figure.

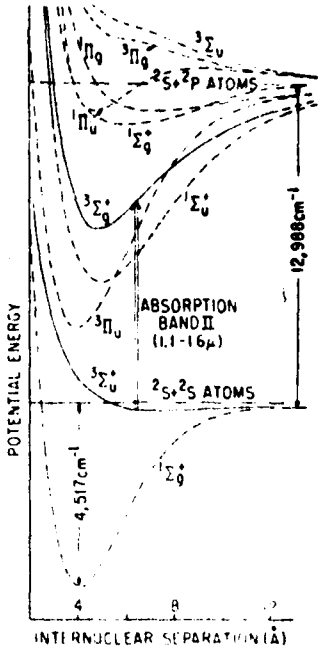

FIG. 3. Qualitative sketch of the electronic potential curves of K_2 based on the recent calculations (Ref. 6) for Li_2. The assignment of the new infrared band II is indicated.

of n potassium atoms into a configuration for which an electronic transition of wavelength λ 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[5]

$$\alpha_2(\lambda, T) = 2\pi^2 r_e c f (g\cdot 4)\nu^{-2} \int dr\, d\nu |N_K|^2 \cdot \exp[-V(\lambda)/RT], \quad (5)$$

where r_e 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 (1) and the ideal-gas law we write

$$\ln(N_K/N_0) = \ln P - \ln(RT) = \ln[P_0/(RT_0)] - (\epsilon/RT) - 1, \quad (6)$$

where the latent internal energy of vaporization ϵ is related to the latent heat l by $\epsilon = l - RT_0 = 18.4$ kcal-mole. P_0 is a constant, N_0 is Avagadro's number, and $T_0 = 943°K$ is a representative temperature which characterizes the conditions of our experiments. Thus, Eq. (4) can be written as

$$\alpha_n(\lambda, T) = c(\lambda)\exp[-(n\epsilon + V)/RT]. \quad (7)$$

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

$$E(\lambda) = n\epsilon + V. \quad (8)$$

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 ($\lambda < 1.1$ μm) 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_2 dimers. The association energy of ~ 1 kcal/mole corresponds approximately to the ~ 1 eV dissociation energy of the $K_2(^1\Sigma_g^+)$ ground-state molecule. The potential energy curves for K_2 are shown in Fig. 3.

Band II (1.1 μm ≲ λ ≲ 1.6 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 2ϵ of two potassium atoms is 36.8 kcal/mole. The difference, 3.2 kcal/mole, can be interpreted as a repulsive interaction potential between a pair of ground-state K atoms on the $^3\Sigma_u^+$ potential curve. Theoretical calculations[6] for Li_2 suggest that the transition $(^3\Sigma_u^+ - {}^3\Sigma_g^+)$ 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 alkali atom (7665–7699 Å for K). It is reasonable to identify the observed knee at 1.58 μm in Fig. 2 with the predicted satellite.

The observed magnitude of the attenuation coefficient of band II is also consistent with the value expected for the transition $(^3\Sigma_u^+ - {}^3\Sigma_g^+)$. Using Eq. (5), and substituting therein the following reasonable values: $\alpha = 1$, $g = 3$, $r = 8$ Å, $dv/dr = 5 \times 10^{21}$ sec^{-1} cm^{-1}, $N_K = 3 \times 10^{16}$, and $V = E(1.2\ \mu m) - 2\epsilon = 37.5 - 36.8 = 0.7$ kcal/mole, we find $\alpha_2(1.2\ \mu m, 943°K) = 0.6$ cm^{-1}, a number 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 of band II all support the assignment of this band to the transition $(^3\Sigma_u^+ - {}^3\Sigma_g^+)$.

Band III ($\lambda \gtrsim 1.6$ μm) is about a factor of 70 weaker than band II and it has a substantially higher activation energy ($E \gtrsim 56$ kcal/mole). If we attempt to assign band III to a dimer transition we must interpret the high activation energy, $E(1.8\ \mu m) = 56$ kcal/mole, as a repulsive potential energy ~ 19.2 kcal/mole. For example, one might try to assign band III to the transition of electronic excited II state to $^3\Sigma_g^+$. However, the measured magnitude of the absorption coefficient in band III is about 300 times too big to be consistent with dimer absorption and any reasonable values of the 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 3ϵ = 55.2 kcal/mole. Thus, loosely bound alkali trimers are a possible source of the absorption in band III. The "number density" c of oscillator electrons involved in the absorption band is related to the strength, $S = \int \alpha dv$, of that band by the well known formula $c = S\ \pi r_e c$. For band III (integrating from 1.6–2.0 μm) we estimate c to be about 5.6×10^{12} cm^{-3}. The total number density of valence electrons in the vapor is very nearly equal to the potassium-atom number density $N_K = 3 \times 10^{16}$. The fraction of valence electrons involved in band III is therefore 1.9×10^{-6}. 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 $N_{K_3} \sim c \sim a^6 N_K^3$ where a is a characteristic internuclear separation for the cluster of three potassium atoms. Using the estimates $c = 1.9 \times 10^{-6}$ and $N_K = 3 \times 10^{16}$ we find a 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_3 is known from theoretical calculations[7] to have low-lying electronic potential surfaces between which fully allowed electronic transitions are possible; for example, the $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states of $D_{\infty h}$ 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)[8] 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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APPENDIX B

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LASER-EXCITED CROSS FLUORESCENT EMISSION FROM CESIUM MOLECULES *

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Received 5 February 1979

We report the first observation of cross fluorescent infrared emission bands from laser-excited alkali molecules. One example, a newly observed band of Cs_2 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, 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 1μ. 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

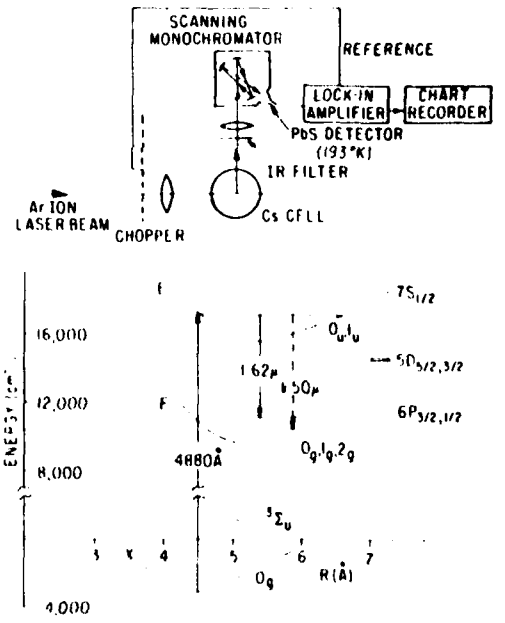

Fig. 1 (a) Apparatus. (b) Schematic diagram of the potential curves involved in infrared cross fluorescence of Cs_2 molecules. The states designated by F and F may actually be several independent molecular states and the only possible quantum numbers of these states are indicated. The radiation at 1.62 μ corresponds to the distance of closest approach of the curves F and I. The radiation at 1.505 μ may be associated with a different final state I or initial state F.

* This work was supported by the U.S. Army Research Office (Durham) under Grant DAAG29-77-G-0015, with supplemental support by the Joint Services Electronics Program (U.S. Army, U.S. Navy, and U.S. Air Force) under Contract DAAG29-77-C-0019.

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 ($\approx$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] $\approx 10^{15}$ cm^{-3} and short excited-state lifetimes [3] $\tau \lesssim 27$ 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

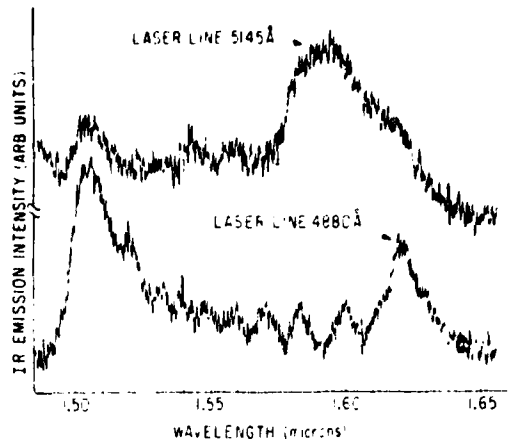

Fig. 2. Cross fluorescent infrared emission bands from laser-excited Cs_2 molecules.

near the bottom of the $X\,^1\Sigma_g$ ground state of Cs_2. The upper state, which we denote by E 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 E in fig. 1b. Since the ground-state symmetry is 0_g the E-state symmetry must be 0_u or 1_u. The E 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 cm^{-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 $^1\Pi_g$, $^3\Pi_g$, $^1\Sigma_g$ and $^3\Sigma_g$ 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 L–S coupling mainly as an convenient bookkeeping device.

We have been unable to find any published information, theoretical or experimental, on the location of the gerade states of the 6P, 6S manifold of Cs_2. However, 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 $^1\Pi_g$ and $^1\Sigma_g$ can be expected to have weakly attractive potential curves of the type, sketched in fig. 1b which would be consistent with our observation.

The pronounced undulatory structure of the emission bands in fig. 2 is similar to the expected spectrum for Condon internal diffraction [7]. The long wavelength peak at 1.62 μ would then be a satellite corresponding to a minimum in the difference potential between states F and F. The fact that the infrared band stops beyond 1.62 μ for both 4880 Å and 5145 Å excitation even though the overall band shapes are very different supports the identification of 1.62 μ as the wavelength of a satellite or head of heads. The nature of the peak at 1.505 μ is less clear. Although one might be tempted to assign the emission at 1.505 μ to emission from a turning point in the potential E, the fact that a peak at 1.505 μ is also present for 5145 Å excitation argues against such an interpretation since one would expect different vibrational states and hence different turning points to be produced by different excitation lines. Another possibility is that the peak at 1.505 μ is a second satellite corresponding to the same or a different pair of states E and F. A detailed assignment of the new infrared bands must await the accumulation of more experimental data.

We have observed very similar infrared emission bands in Rb_2 dimers, excited into the C state by 4880 Å and 4765 Å lines from the Ar^+ laser [8]. It is reasonable to expect analogous infrared emission bands to exist 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 dissociate into excited and ground state atoms. Cross fluorescence can be as important as predissociation in leading to excited atoms under collision-free conditions. Since we have discovered that cross fluorescent infrared 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 observations of cross fluorescent decay modes for alkali dimers. This establishes the existence of an important and previously ignored decay channel which should be considered 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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APPENDIX C

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Visible Emission Bands of KXe_n Polyatomic Exciplexes

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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_n 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 S 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-A 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)-A 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 A, which is known[3] to be an emission band of potassium monoxenide KXe(5S) $-$ KXe(4S), and a broad assymetric emission band between 5300 and 7000 A which we attribute to the superposed emission bands of polyatomic exciplexes: $KXe_n(5S) - KXe_n(4S)$ 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 5750 Å for $[Xe] = 0.9$ 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 $S(\lambda, [Xe], T)$ of the polyxenide band to the monoxenide band by

$$S(\lambda, [Xe], T) = \frac{I(\lambda, [Xe], T) - \alpha I(\lambda, [Xe]_0, T)}{\alpha I(\lambda_0, [Xe]_0, T)}, \quad (1)$$

where λ_0 is the wavelength of the peak of the monoxenide band, and the constant α is defined by

$$\frac{I(\lambda, [Xe], T)}{I(\lambda, [Xe]_0, T)} = \alpha \text{ for } \lambda \approx 5220 \text{ A}. \quad (2)$$

Here $I(\lambda, [Xe]_0, T)$ 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 $[Xe] \approx 0.9$ amagat, and so we can take $I(\lambda, [Xe]_0, T)$ as the fluorescence spectrum at $[Xe] \approx 0.9$ amagat.

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

$$S(\lambda, [Xe], T) = W(\lambda, [Xe]) \exp[E(\lambda)/kT]. \quad (3)$$

Some typical plots of $\ln S(\lambda, [Xe], T)$ versus $1/T$ are shown in Fig. 2(b). The slopes of the straight lines in Fig. 2(b) are proportional to the energies $E(\lambda)$. We have made plots similar to those of Fig. 2 for xenon densities of 11.4, 8.4, 8.1, 6.6, 6.4, 5.4, and 4.0 amagats. We find that the energies $E(\lambda)$ are independent of the xenon density to within our experimental accuracy of $\pm 5\%$, and they can be well represented by the empirical formula

$$E(\lambda) = 2.125\lambda - 10675, \quad (4)$$

with $E(\lambda)$ in cm^{-1} and λ 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 $W(\lambda, [Xe])$ of Eq. (3) have a power-law dependence on the xenon density,

$$W(\lambda, [Xe]) = [Xe]^{n(\lambda)-1} G(\lambda), \quad (5)$$

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

$$n(\lambda) - 1 = 1.74 \times 10^{-3}\lambda - 8.23 \quad (6)$$

with λ in angstroms.

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

$$G(\lambda) = 1778.5 - 0.668\lambda + 6.28 \times 10^{-5}\lambda^2. \quad (7)$$

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

$$S(\lambda, [Xe], T) = G(\lambda)[Xe]^{n(\lambda)-1} \exp[E(\lambda)/kT]. \quad (8)$$

The parameters, $E(\lambda)$, $n(\lambda)$, and $G(\lambda)$ 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 KXe_n has a characteristic emission band, similar to but broader than the

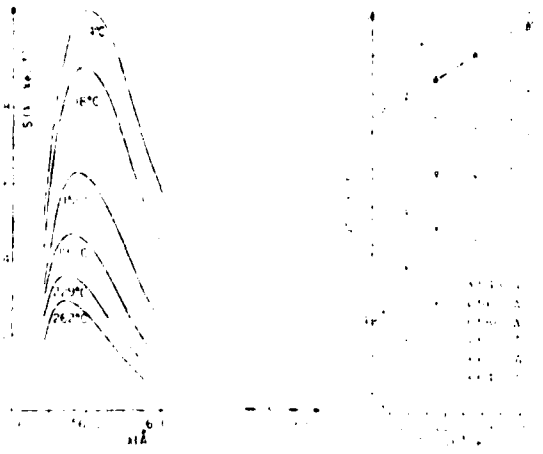

FIG. 2. (a) Spectra of the polyxenide component at a xenon density of 8.4 amagats, measured at various temperatures. The polyxenide spectra are obtained by subtracting the monoxenide component from the original data and then normalizing to the amplitude of the monoxenide peak. (b) The logarithm of the polyxenide component is shown plotted against the reciprocal of the absolute temperature for several different fluorescence wavelengths.

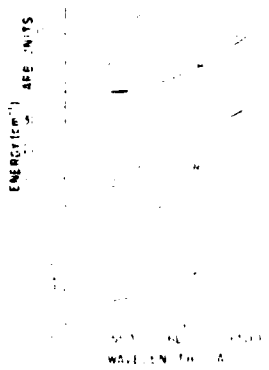

FIG. 3. Experimentally determined empirical functions $n(\lambda)$, $E(\lambda)$, and $G(\lambda)$. The function $B(\lambda)$, representing the binding energy per xenon atom, and a typical polyxenide line shape $S(\lambda)$ are also shown.

monoxenide band, for integral values of n ($n = 2, 3, 4, \ldots$). The peaks of the emission bands of KXe_n shift systematically to longer wavelengths for increasing values of n. A large part of the red shift is due to the binding energy of Xe atoms to K(5S). The polyxenide bands of Fig. 2 therefore consist of the superposed and unresolved emission bands of KXe_2, KXe_3, KXe_4, etc. Collisional rates are very fast in the high density systems we are studying (two-body collision rate is $\sim 10^{10}$ sec^{-1}, and three-body collision rate is $\sim 10^{7}$ to 10^{9} sec^{-1} for a xenon density of 10^{20} 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 $KXe_n(5S)$ for n being 2, 3, ... Therefore we expect the intensity of the emission band due to KXe_n to be proportional to $[Xe]^n$. Since there is substantial overlap of these bands the apparent density dependence of the fluorescence of wavelength λ is $[Xe]^{n(\lambda)}$ where $n(\lambda)$ is the measured noninteger exponent represented by the empirical formula (6). In this interpretation the exponent $n(\lambda)$ is the average number of xenon atoms attached to a potassium atom when the fluorescent wavelength is λ. The values λ_p defined by $n(\lambda_p) = p$ with $p = 2, 3, 4$, etc., can be identified approximately as the peak wavelengths of the emission bands of KXe_2, KXe_3, KXe_4, etc. From Fig. 3 we see that $\lambda_2 = 5500$, $\lambda_3 = 5900$, and $\lambda_4 = 6400$ Å. The peak of the well-resolved monoxenide spectrum occurs at $\lambda_1 = 5220$ Å.

The energy $E(\lambda)$ 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

$$KXe(5S) + (n-1)Xe - KXe_n(5S) + E. \quad (9)$$

We may define a quantity $B(\lambda)$ by

$$B(\lambda) = E(\lambda)\,|n(\lambda) - 1|, \quad (10)$$

and we shall call $B(\lambda)$ 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 $B(\lambda)$, 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 $kT \sim 300$ 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 $G(\lambda)$ is perhaps the most remarkable property of the polyxenide band. The function $G(\lambda)$ 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 n, the rapid growth of $G(\lambda)$ with increasing λ must be due to an increase 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 $KXe_n(5S)$ 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 prominence 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.[4] Since the first excited P states of free alkali atoms have fully allowed transition rates to the ground state, they can only be weakened by multiple-perturber effects, while forbidden lines are strongly enhanced.

The nature of these polyxenide exciplexes is

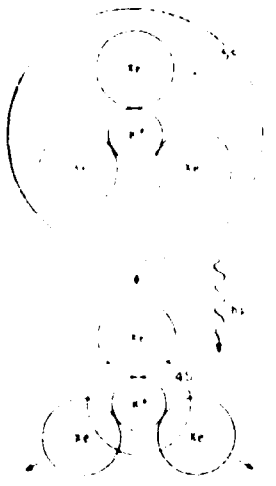

FIG. 4. Schematic representation of the physical dimensions of potassium polyxenide molecules. The ionic core of K^+ has a radius of $2.5a_B$ (a_B = Bohr radius) and a xenon atom has a radius, $3.6a_B$. For the 5S state of potassium the mean radius of the electron charge distribution is $11.8a_B$, so 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 $4.7a_B$, and the Xe atoms are no longer bound.

still uncertain, but it is interesting to note that cluster ions of the form $K^+(H_2O)_n$ have been extensively studied,[1-6] and six or more waters of hydration are observed by mass-spectroscopic techniques. Similar bonding of alkali ions to other neutral molecules (O_2, N_2, and CO_2) has been observed[7] and calculated theoretically.[8] The highly polarizable noble gas xenon ($\alpha = 4$ Å^3) can be expected to form analogous cluster ions K^+Xe_n, 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 sketch to indicate the dimensions of such a system is shown in Fig. 4.

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