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Emission spectrum of XeI* in electron-beam–excited Xe/I_2 mixtures*

J. J. Ewing and C. A. Brau
Avco Everett Research Laboratory, Inc., Everett, Massachusetts 02178

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Emission spectra observed from electron-beam–excited atmospheric-pressure gas mixtures of Xe and I_2 are reported and analyzed in terms of an ionic alkali-halide-like excited state Xe^+I^-. A simple theory is given to analyze the observed spectra, and predictions of the uv spectra of other inert-gas monohalides are made. This class of molecules appears to offer interesting possibilities for production of new uv lasers.

INTRODUCTION

This paper describes the continuum emission spectrum of XeI^* which is produced when mixtures of Ar/Xe/I_2 are irradiated with a high-intensity electron beam. A narrow band near 2535 Å is observed and assigned to the transition $(XeI)^*(^2\Sigma_{1/2}) \rightarrow XeI(^2\Sigma_{1/2})$. XeI is an unstable species which rapidly decays into Xe and I. Broader bands are observed at longer wavelengths, 3190 and 3610 Å, and are assigned to transitions which terminate on the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states of XeI. XeI^* is a prototype of a set of inert-gas monohalides which should show similar emission continua in the ultraviolet region.[1]

A simple ionic-bonding model is used to predict that the primarily ionic molecule, Xe^+I^-, an excited state of XeI, is bound with respect to Xe and electronically excited $I(6s\,^4P)$. This "ionic" xenon halide, formed in our high-pressure experiments by rapid energy transfer and three-body processes, can radiate to the repulsive ground-state potentials of XeI. The ionic model can be used to estimate the binding energy of XeI^* as well as the wavelengths of the emission bands which terminate on the repulsive lower-lying states. The diabatic Coulomb potential curve of Xe^+I^- crosses the $Xe + I^*$ potential curve at fairly large internuclear separations as shown in Fig. 1. This is not surprising since Xe^* has an ionization energy comparable to the ionization energy of Cs, which forms ionic molecules with halogens. The large Coulomb binding energy leads to very large shifts in the molecular XeI spectra from the free-atom spectra. Such molecular emission bands could be ideal for an "excimer" or "molecular association" laser. XeI is not unique in this respect, and we make predictions of the approximate wavelengths for similar emission bands for other inert-gas halides.

EXPERIMENTAL DETAILS

Room-temperature mixtures of I_2 with Ar containing 8.5% Xe (total impurity limits ~5 ppm) and also I_2 with pure Xe (50-ppm impurities) were irradiated with a 0.4-MeV electron beam. The $1\times15\text{-cm}^2$ beam was produced by pulse charging a carbon cathode with a Marx generator (Ion Physics Corp.). The energy incident on the test gas is roughly 1 J/cm^2. The pulse time is 100 nsec. The primary electrons ionize and excite the Ar and Xe. This excitation eventually resides in the most bound excited electronic state which then radiates or is quenched. The kinetics of the latter is not yet known for Xe-I_2 mixtures, but three-body processes will be rapid at the pressures used and recombination into bound excited states occurs on a time scale of nanoseconds. Emission spectra were recorded on film (Kodak 103-O) using an *f*/3.5 Hilger quartz prism spectrograph with an entrance slit width of 100 μm; one to three shots gave sufficient film blackening. Time-resolved emission was observed with a 1P28 photomultiplier viewing the exit slit of a Spex 100-mm Micromate monochromator with a bandpass of typically 40 Å.

Figure 2 shows the emission spectrum of 25 lb/in.^{2} (absolute) of 8.5% Xe/Ar inert gas mixed with room temperature I_2 (density ~10^{16} cm^{-3}). These continuum bands do not appear when Ar/I_2 mixes are excited with the electron beam. Similarly, when mixtures of Xe and Ar or pure Xe without I_2 are irradiated, the continua are not observed.[2] Finally when pure Xe is mixed with I_2, the continuum bands are recovered. No evidence has been found on film or by photomultiplier of I_2 emission in the visible or uv. Since the continua require both I_2 and Xe but do not appear in Ar/I_2 mixtures, we conclude that they must arise from a xenon-iodine atom complex. Finally under the conditions of our experiment we do not anticipate that the I_2 will exist for very long during the electron-beam pulse. I_2 will be removed by the processes of energy transfer from Xe^* and Xe_2^*, dissociative attachment by the slow electrons and photodissociation in the visible and most especially in the vacuum uv, where the Xe_2^* excimer band overlaps the I_2 $(X \rightarrow I)$ band.[3] Experimental study and detailed computer modeling of the kinetics of

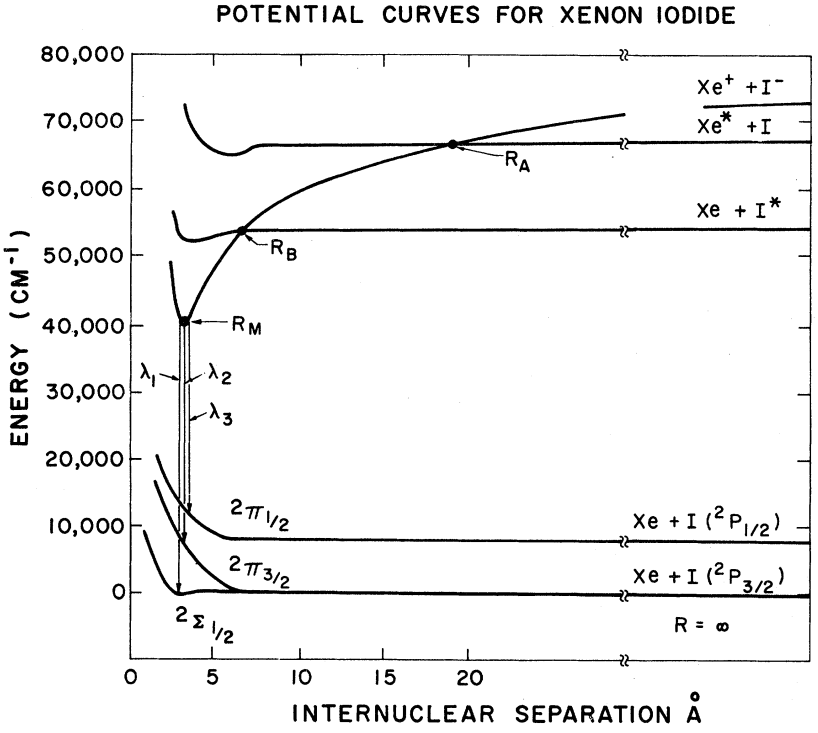

FIG. 1. Estimated potential curves for XeI.

these processes are currently under way.

The emission band at 2535 Å has a fairly sharp edge at ~2549 Å, and about 95% of the emission is found between about 2510 and 2549 Å. This band is noticeably asymmetric and shades off into the blue, indicating that the lower-state potential energy curve for this bound-to-free transition is not changing rapidly with internuclear separation. The 3190 and 3610-Å bands are broad and fairly symmetric, being ~1500 and 4120 cm^{-1} wide, respectively, probably terminating on strongly repulsive lower-state potentials.

IONIC MODEL FOR XeI*

The spectrum observed can be interpreted by the potential energy diagram shown in Fig. 1.

At infinite internuclear separation one has Xe +I($^2P_{3/2}$) at zero energy, Xe +I($^2P_{1/2}$) at 7819 cm^{-1}, Xe +I(^4P) at 54633 cm^{-1} (labeled as Xe +I*), Xe($^3P_2$) +I($^2P_{3/2}$) at 67078 cm^{-1} (labeled as Xe* +I), and Xe$^+$ +I$^-$ at 73128 cm^{-1}. Xe$^+$ +I$^-$ is lower in energy than Xe$^+$ + e +I by an amount equal to the electron affinity of iodine.[4] For simplicity, only the lowest-lying excited states are shown. As R decreases the low-lying ^2P states are split into $^2\Sigma_{1/2}$, $^2\Pi_{3/2}$, and $^2\Pi_{1/2}$ states.[3] These molecular potentials should be repulsive at small R. The $^2\Sigma_{1/2}$ state lies lowest since the p orbital hole on the I atom points directly at the electron-rich Xe atom. The $^2\Pi$ states, however, put two p electrons in the immediate vicinity of Xe and hence should be considerably more repulsive than the $^2\Sigma_{1/2}$ state.

Similarly the ^2P Xe$^+$ and the ^1S I$^-$ ions will produce $^2\Sigma_{1/2}$ and $^2\Pi_{1/2,3/2}$ states having the same order as the lower states for similar reasons. At

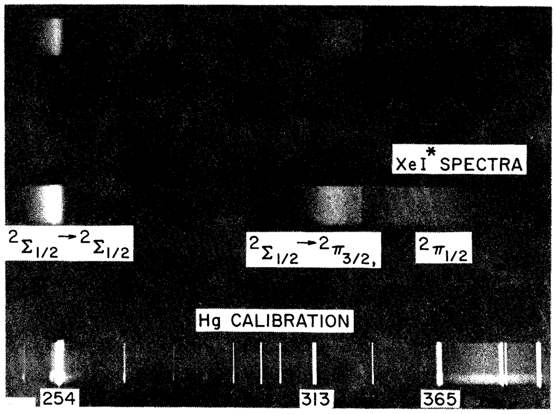

FIG. 2. Emission spectra of Ar/Xe/I$_2$ mixes. Top, 1 shot; middle, 3 shots; bottom, Hg calibration.

the minimum of the ionic curve, the ${}^2\Pi$ states of XeI* will probably be more than kT higher in energy than the ${}^2\Sigma$ ion state. At large R the energy of the ion pair is readily estimated by simple Coulomb attraction, while the Xe + I* and Xe* + I potential curves are flat. The zero-order ionic curve will cross, in a diabatic sense, all of the Xe* + I and I* + Xe curves at fairly large values of R, as in the more familiar case of alkali halide molecules.[5]

Table I lists the values of R at which these crossings occur for XeI and other inert gas monohalides. The crossing radii, in atomic units, are given by the expressions $R_A^{-1} = V_I(\mathrm{Xe}^*) - \mathrm{EA(I)}$ and $R_B^{-1} = V_I - \mathrm{EA} + E_D$, where V_I is the ionization potential of the Xe excited state, EA the electron affinity of iodine, and E_D the energy gap between Xe* + I and Xe + I*, all energies being expressed in atomic units. These derive from the simple condition that the attractive Coulomb energy e^2/R be equal to the energy difference at infinite separation. Any deviation from flatness of the covalent potential or deviation from pure Coulombic attraction for the ion pair will alter this result of course. Deviations can be expected for crossings which would occur at small R. The closer crossing, R_B, may never occur for some of the inert-gas monohalides such as ArI. For XeI*, R_A and R_B are sufficiently large that the lowest excited state potential will be predominantly ionic in nature.

The ionic curve drops in energy to R_M, where short-range repulsion becomes important. We estimate R_M and E_M by noting that the nearly isoelectronic salt CsI has comparable ionic binding, and that Cs^+ and Xe^+ ions should have about the same size. R_M for gaseous CsI is 3.32 Å,[6] and the binding energy relative to ions is 97.4 kcal/mole.[7] Subtracting the CsI binding energy from $E\ (\mathrm{Xe}^+ + \mathrm{I}^-)$ gives E_M of 39135 cm^{-1}. E_M would be 39135 cm^{-1}. Using this E_M one predicts emission to occur at 2555 Å if the lower ${}^2\Sigma_{1/2}$ state has zero energy at R_M. Since the 2535-Å band is very narrow and has a sharp long-wavelength edge, the presumption that the lower ${}^2\Sigma$ state is flat at R_M is probably good. The predicted emission wavelength is within 1% of observed; so for estimating the spectra of other inert gas monohalides we will use the binding energy of the nearest alkali halide. The observed ${}^2\Sigma \rightarrow {}^2\Sigma$ band position and shape implies E_M (XeI*) is actually 39 450 cm^{-1}.

One can use the observed positions and spectral widths of the XeI* bands to estimate the lower-state energies and potential gradients at R_M. In the upper state roughly 95% of the molecules will be in vibrational states. $v = 0, \ldots, 4$, assuming a vibrational temperature of 300°K. Using the molecular constants of CsI, we estimate the spread in R accessible to the XeI* molecules from the rms value of $(R - R_M)/R_M$ for a harmonic oscillator,

TABLE I. Estimated features of inert-gas monohalides.

Molecule	R_A (Å)	R_B (Å)	R_M (Å)	E_M (cm^{-1})	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)
XeI	19.2	6.3	3.3	39 135	256	302	342
XeBr	32.0	15.9	3.1	34 272	292	354	407
XeCl	71.9	a	2.9	30 860	324	402	417
XeF	39.6	a	2.35	25 895	386	503	512
KrI[b]	14.1	3.5	3.2	54 000	185	208	247
KrBr	19.9	5.2	2.9	49 353	203	231	252
KrCl	30.5	9.8	2.8	45 592	219	253	258
KrF	22.7	a	2.27	39 229	256	301	305
ArBr[c,b]	17.0	3.2	2.8	62 152	161	178	190
ArCl[c,d]	24.1	4.5	2.7	58 042	172	192	195
ArF[c]	18.9	a	2.17	37 484	267	318	322
NeF[c,b,e]	9.6	2.6	1.93	93 266	107	115	115

[a] These species have halogen excited-state levels only above the inert-gas excitation levels. Hence no R_B crossing occurs.

[b] These species will not be as "ionic" as those with large R_B.

[c] These spectra could be complicated due to multiple excited states because of the smaller spin orbit splitting in Ar^+ and Ne^+.

[d] The ArCl bands appear at 170 nm (λ_1) and 175 nm (λ_2, λ_3) in low-pressure discharge flow experiments, Ref. 9; λ_1 apparently is predicted within 1% while λ_2, λ_3 are within 10%.

[e] For ArI, NeI, NeBr, NeCl, and the helium halides the inert-gas ionization potential is so large that the Coulomb curve does not make up sufficient energy to approach the low-lying halogen excited states. These compounds should only have small well depths and the molecular continua should be near the free atom lines. Possibly ionic states of the opposite polarity, viz. $\mathrm{Ne}^- + \mathrm{I}^+$, could enter into the binding.

$[2B\omega^{-1}(v+\frac{1}{2})]^{1/2}$, apparently an adequate estimate for the alkali halides.[8] We calculate a total R width of 0.3 Å for $v=4$. From the plates, we estimate the 95% widths to be 650 cm^{-1}, 1500 cm^{-1}, and 4120 cm^{-1}. The width of the bands in excess of $2kT$ is attributable to a slope in the lower-state potential curve. For $^2\Sigma_{1/2}$ the slope is about 670 cm^{-1} Å^{-1}, again indicating that this state is not in the region of strong repulsion at R_M. The $^2\Pi_{3/2}$ slope is estimated to be 5000 cm^{-1} Å^{-1}, $^2\Pi_{1/2}$ is 13 700 cm^{-1} Å^{-1}. We do not understand why the $^2\Pi_{1/2}$ band is broader.

The center of the $^2\Pi$ bands locates the energies of these repulsive states at R_M. $^2\Pi_{3/2}$ is at about 8100 cm^{-1}, while $^2\Pi_{1/2}$ is ~4150 cm^{-1} above its separated-atom limit of $^2P_{1/2}$.

These pieces of information then can be used to make crude estimates of the emission spectra of the other inert-gas monohalides as given in Table I. The rules for obtaining Table I are: E_M is determined by subtracting the bond energy of the nearest alkali halide from the infinite-R ion pair energy (CsBr is used for XeBr*, etc.); R_A and R_B are obtained by assuming the covalent potentials are flat for all R; the $^2\Sigma \rightarrow {}^2\Sigma$ band position is estimated by assuming the $^2\Sigma_{1/2}$ ground state has zero energy at R_M; the $^2\Pi$ states energies at R_M are estimated to be 6000 cm^{-1} (the average of our $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ XeI repulsions) above their respective infinite-separation values. We feel these estimates will predict the emission wavelengths to within 10%, and future measurements should give better estimates of the potentials of other inert-gas halides.

Note added. Since the submission of this paper a communication by Velazco and Setser[10] has appeared substantially confirming the predictions for the $\Sigma \rightarrow \Sigma$ bands of XeCl, XeBr, and XeF. Peak wavelengths appear at: XeI, 252 nm; XeBr, 278 nm; XeCl, 304 nm; and XeF, 346 nm. The spectra they observe are broader since their work is done at low pressures and they observe emission from species which do not have time to vibrationally relax before emitting uv photons. The peak wavelengths are in agreement with recent data on these species obtained in our high-pressure experiments. Also a paper by Golde and Thrush[11] on ArCl emission has appeared making many of the same arguments about the ionic binding in this molecule. As pointed out in the table, the wavelength for ArCl emission is in good agreement with our prediction for the $\Sigma \rightarrow \Sigma$ transition.

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[2] We do see the XeO "auroral line" continua in the green, and an unidentified band near 3290 Å when "pure" Ar/Xe or Xe is excited with the electron beam.

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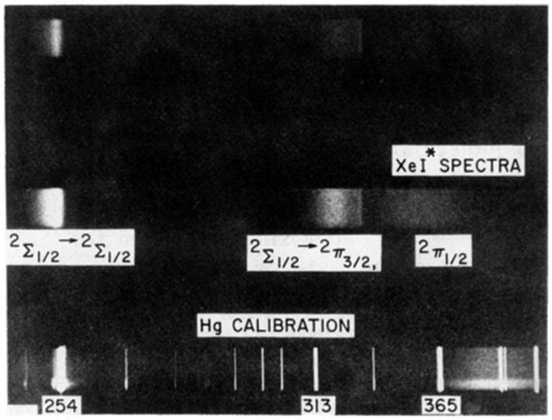

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