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**Abstract:**
Experimental kinetic measurements were made for mercury and mercury halide systems that have relevance for mercury halide lasers operating on the B-X transitions. The quenching of Hg(3P₂) atoms by halogens, the vibrational relaxation of HgCl(B) and HgBr(B), and the dissociative excitation transfer from N₂(A) and Xe(3P₂, 1) to HgCl₂, HgBr₂, CH₃HgCl, CH₃HgBr and CH₃HgI were studied. In addition, relaxation processes in the triplet states of N₂ were investigated; the very facile coupling between the N₂(W) and N₂(B) states was discovered and studied at the state-to-state level.
FINAL REPORT

EXCITED STATE KINETICS OF MERCURY HALIDES AND MIXTURES WITH N₂ AND Xe.

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Summary

Experimental kinetic measurements were made for mercury and mercury halide systems that have relevance for mercury halide lasers operating on the B-X transitions. The quenching of Hg(3P₂) atoms by halogens, the vibrational relaxation of HgCl(B) and HgBr(B), and the dissociative excitation transfer from N₂(A) and Xe(3P₂,₁) to HgCl₂, HgBr₂, CH₃HgCl, CH₃HgBr and CH₃HgI were studied. In addition, relaxation processes in the triplet states of N₂ were investigated; the very facile coupling between the N₂(W) and N₂(B) states was discovered and studied at the state-to-state level. The coupling to N₂(B') also is important for some N₂(B) vibrational levels. Perhaps the most interesting feature discovered from the Hg(3P₂) atom studies was the very high branching fraction for formation of excited state mercury halides in reaction with molecular halogens, which is in strong contrast with the reactions of the lower Hg(3P₁) and Hg(3P₀) states. Since our work either has been published or is in manuscript form, this final report is presented in the form of a listing of abstracts of papers that have been or soon will be published. The listing is given in three categories.

I) Excited state kinetics of N₂(A), N₂(B) and excitation-transfer reactions to Mercury (II) halides.

II) Quenching and excitation transfer reactions of metastable rare gas atoms with HgX₂ and Hg.

III) State-to-state kinetics for quenching of Hg(3P₂) atoms by halogen containing molecules and vibrational relaxation of HgCl(B) and HgBr(B).
I. Excited State Kinetics of \( N_2(A^3\Sigma_u^+) \), \( N_2(B^3\Pi_g) \) and Excitation Transfer Reactions to HgX \(_2\) Molecules.

1) PRODUCTION OF THE \( N_2 \) HERMAN INFRARED SYSTEM BY THE ENERGY POOLING REACTION OF \( N_2(A^3\Sigma_u^+) \) METASTABLE NITROGEN MOLECULES


Molecular \( N_2 \) emission, observed from an \( Ar(3P_0) \) and \( Xe(3P_2) \) flowing afterglow apparatus, indicates that the energy pooling reaction by \( 2N_2(A^3\Sigma_u^+) \) generates the emission from the Herman infrared system, which is an unassigned nitrogen band system. A lower limit to the formation rate constant for the upper state of the Hermann infrared system was found to be \( 2.5 \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). The information presented here may help in the identification of the upper and lower states of the emission system. The \( 2N_2(A) \) energy pooling reaction also forms \( N_2(B^3\Pi_g, v>8) \) but a rate constant cannot be assigned from the present data.

2) ENERGY TRANSFER REACTIONS OF \( N_2(A^3\Sigma_u^+) \). 5. QUENCHING BY HYDROGEN HALIDES, METHYL HALIDES, AND OTHER MOLEULES


The 300 K quenching rate constants for \( N_2(A^3\Sigma_u^+, v'=0,1) \) have been measured with 20 small molecules, mostly of the hydrogen halide or methyl halide variety. The metastable \( N_2(A) \) molecules were prepared by the reaction of \( Ar(3P_0) \) with \( N_2 \) in a discharge-flow system. Rate constants were measured by observing the variation of the \( N_2(A^3\Sigma_u^+ - X^1\Sigma_g^+) \) emission intensity as a function of added reagent concentration. The magnitude of the rate constants increase in the \( HX \) and \( CH_3X \) series as \( X \) changes from F to I. The temperature dependence of the \( NO, O_2, C_2H_2, \) and \( C_2H_4 \) reactions were qualitatively investigated with the discharge flow technique by comparing experiments at \( \sim 120 \) and 300 K. On the basis of the limited data, the rate constants are either virtually invariant with temperature or decrease mildly with decreasing temperature. In contrast the \( N_2(A) \) bimolecular, energy pooling, \( N_2(C) \) formation rate constant appears to increase with decreasing temperature. The results of the present study are compared to previous investigations from this laboratory and to other studies of \( N_2(A^3\Sigma_u^+) \).

3) QUENCHING OF \( N_2(A^3\Sigma_u^+) \) BY Hg(II) HALIDES


The flowing afterglow technique has been used to study the reactions of \( N_2(A^3\Sigma_u^+, v=0,1) \) with some methylmercury and mercuric halides. Room temperature quenching rate constants and rate constants for production of \( HgX(B^2\Sigma_g^+) \) were measured. Evidence is presented that shows another electronic state of \( N_2 \), besides \( N_2(A) \), can produce \( HgX(B) \) via dissociative excitation reactions with \( HgX_2 \).
4) **COLLISIONAL COUPLING OF \( \text{N}_2(\text{B}^3\Pi_{\text{g}}) \) AND \( \text{N}_2(\text{W}^3\Delta_{\text{u}}) \) STATES: STUDIED BY LASER-INDUCED FLUORESCENCE**


The \( \text{N}_2(\text{B}^3\Pi_{\text{g}}) \) state was produced by laser excitation of \( \text{N}_2(\text{A}^3\Pi_{\text{g}}) \) in Ne or Ar carrier gas in a flowing afterglow apparatus. All of the vibrational levels initially populated by the laser, \( v' = 3-10 \), showed double exponential relaxation. The initial fast decay is associated with collisional coupling of the \( \text{N}_2(\text{B},v') \) level to adjacent \( \text{N}_2(\text{W}^3\Delta_{\text{u}}) \) vibrational levels. The slow decay represents the overall decay of these coupled levels, which generates lower vibrational levels of \( \text{N}_2(\text{B}^3\Pi_{\text{g}}) \).

5) **PRIMARY \( \text{N}_2(B) \) VIBRATIONAL DISTRIBUTIONS FROM EXCITATION-TRANSFER REACTIONS BETWEEN \( \text{Kr}(\text{P}_2) \) OR \( \text{Xe}(\text{P}_2) \) ATOMS AND \( \text{N}_2 \)**


Low-pressure flowing afterglow experiments with Ne carrier gas have been performed to obtain the initial \( \text{N}_2(B) \) vibrational distributions and the \( \text{N}_2(B) \) formation rate constants for \( \text{Xe}(\text{P}_2) \) and \( \text{Kr}(\text{P}_2) \) excitation-transfer reactions to \( \text{N}_2 \). The \( \text{N}_2(C) \) formation rate constant for \( \text{Ar}(\text{P}_2) + \text{N}_2 \) also was measured. The results are consistent with a very specific interaction mechanism favoring only a few of the many available \( \text{N}_2^* \) exit channels.

6) **COLLISIONAL COUPLING AND RELAXATION OF \( \text{N}_2(\text{B}^3\Pi_{\text{g}}) \) AND \( \text{N}_2(\text{W}^3\Delta_{\text{u}}) \) VIBRATIONAL LEVELS IN Ar AND Ne**


Laser excitation from \( \text{N}_2(\text{A}^3\Sigma^+_2,v=0-6) \) in Ne and Ar carrier gas in a flowing afterglow apparatus has been used to prepare \( \text{N}_2(\text{B}^3\Pi_{\text{g}}) \) molecules in individual levels from \( v'=3-10 \). The subsequent \( \text{N}_2(B-A) \) fluorescence intensity was observed to study the coupling and relaxation kinetics of \( \text{N}_2(B^3\Pi_{\text{g}},v=2-10) \). The decay curves from each level show double (or higher) exponential relaxation. The first component is assigned as primarily the rapid coupling of the \( \text{N}_2(B^3\Pi_{\text{g}},v) \) and \( \text{N}_2(W^3\Delta_{\text{u}},v+1) \) levels, however, the \( \text{N}_2(B^3\Sigma^-,v=4) \) levels also may be involved for \( \text{N}_2(B,v>5) \). The slowest decay component represents the subsequent relaxation of the coupled levels. The combination of the two steps is equivalent to apparent stepwise vibrational relaxation of \( \text{N}_2(B^3\Pi_{\text{g}},v) \); such relaxation occurs even at low Ar pressure because of the large rate constants and long radiative lifetimes of \( \text{N}_2(B) \) and \( \text{N}_2(W) \). The coupling pattern between \( \text{N}_2(B) \) and \( \text{N}_2(W) \) is analyzed, and rate constants are assigned to elementary steps in the relaxation sequence and the scheme is evaluated. From the analysis of the slow decay components in argon, estimates (20-90 \( \mu \)s) are obtained for the radiative lifetimes for the reservoir levels, which are assigned as \( \text{N}_2(W^3\Delta_{\text{u}},v) \) for \( \text{N}_2(B,v<4) \) and \( \text{N}_2(W^3\Delta_{\text{u}},v+1) \) levels and possibly \( \text{N}_2(B^3\Sigma^-_{\text{g}},v=4) \) levels for \( \text{N}_2(B,v>5) \).
II. Quenching and Excitation-Transfer Reactions of Metastable Rare Gas Atoms
with Hg and HgX2-

1) DISSOCIATIVE EXCITATION OF Hg(II) HALIDES BY Xe\(^{3P_2}\) AND Xe\(^{3P_1}\)


Rate constants for the production of excited state products from the reaction of Xe\(^{3P_2}\) with several methylmercury and mercuric halides have been measured in a flowing afterglow at elevated temperatures. The most important product is HgX\(^{1B_Z}\), X = Cl, Br, I for all reagents studied. Minor amount of HgX\(^{1D_3}\) and XeX\(^{1B}\) emission also were observed. Sensitization experiments with Xe\(^{3P_1}\) and HgCl\(_2\) gave the same result. For HgCl\(_2\) and HgBr\(_2\), the HgX\(^{1B}\) formation rate constants are large (\(\sim 10^{-9}\) cm\(^{-1}\) molec\(^{-1}\) sec\(^{-1}\)), which suggests that quenching of Xe gives HgX\(^*\) with a branching ratio of nearly unity. The HgX\(^{1B}\) formation rate constants from CH\(_2\)HgX compounds are about an order of magnitude smaller than for the HgX\(_2\) compounds. Reactions of both CH\(_2\)HgX and HgX\(_2\) compounds with He\(^{2S}\), Ne\(^{3P_2}\), Ar\(^{3P_2}\), and Kr\(^{3P_2}\) gave predominantly Hg emission.

2) QUENCHING RATE CONSTANTS OF METASTABLE ATOMS OF NEON, ARGON, AND KRYPTON
BY MERCURY ATOMS


Room temperature rate constants (thermal average cross-sections) for the quenching of electronically excited state rare gas metastable atoms by mercury atoms have been measured using the flowing afterglow technique. The thermal cross sections are \(\sigma_0[\text{Hg}(^{3P_2})] = 70\ \text{A}^2\); \(\sigma_0[\text{Ar}(^{3P_2})] = 194\ \text{A}^2\); \(\sigma_0[\text{Ar}(^{3P_1})] = 219\ \text{A}^2\); and \(\sigma_0[\text{Kr}(^{3P_2})] = 124\ \text{A}^2\). The mechanism for quenching by mercury atoms is Penning ionization for N\(^*\) and Ar\(^*\) and excitation transfer for Kr\(^*\). These results are discussed in terms of the cross-section of similar reagents and the cross-section predictions of the close collision criteria. The large experimental cross-sections indicate that the total quenching cross-section is dictated by interactions occurring at large internuclear distances associated with a long range attractive potential. However, the interactions at shorter range are responsible for the actual conversion from reactants to products. The Kr\(^{3P_2}\) + Hg excitation transfer reaction provides a way to generate Hg\(^{3P_2}\) metastable atoms in a flowing afterglow apparatus.
III. State-to-State Kinetics for Quenching of Hg\(^{3P_0}\) Atoms by Halogen Containing Molecules and Vibrational Relaxation of HgCl(B) and HgBr(B).

1) A FLOWING AFTERGLOW SOURCE OF Hg\(^{3P_0}\) and Hg\(^{3P_2}\): APPLICATION TO HgX(B), X = F, Cl, Br, I FORMATION KINETICS


Passing a mercury saturated flow of Ar though a low power, hollow-cathode discharge gives Hg\(^{3P_0}\) and Hg\(^{3P_2}\) metastable atom concentration of \(\sim 5 \times 10^5\) atoms cm\(^{-3}\) in a flowing afterglow reactor. The reaction of Hg\(^{3P_2}\) with halogens have been studied by observation of the low pressure, collision-free HgX(B), X = F, Cl, Br and I chemiluminescence. This appears to be the first report of the HgF(B-X) emission spectrum.

2) INTERPRETATIONS OF THE MERCURY HALIDE \((B^2\Sigma^+ - X^2\Sigma^+)\) CHEMILUMINESCENCE FROM REACTIVE QUENCHING OF Hg\(^{3P_2}\) BY HALOGEN CONTAINING MOLECULES


The HgX\((B^2\Sigma^+-X^2\Sigma^+)\), X = halogen, emission spectra have been recorded from Hg\(^{3P_2}\) atom reaction with several halogen containing molecules using a flowing afterglow reactor. The HgX\(^*\) emission intensities were compared with the HgCl\(^*\) emission intensity from Hg\(^{3P_2}\) + Cl\(_2\) to assign rate constants for HgX(B) formation. The Hg\(^{3P_2}\) + diatomic halogen reactions have large k\(_{HgX}\) and their branching fractions for HgX(B) formation are probably unity. The polyatomic reagents generally gave much smaller k\(_{HgX}\); although, a few moderately good donors, e.g., CF\(_3\), CBr\(_4\), CCl\(_4\) and NF\(_3\) were identified. The experimental spectra were numerically simulated to assign HgX(B) vibrational energy distributions. A decrease in \(<f_(HgX)>\) was found for the Cl\(_2\), Br\(_2\), I\(_2\) series which is analogous to previous findings for \(<f(XeX)>\) from reactive quenching of Xe\(^{3P_2}\). Possible reasons for the similarity are discussed. The HgX(B) vibrational energy disposal for polyatomic reagents is compared to analogous data for reaction of alkaline earth metal atoms and Xe\(^{3P_2}\).

3) MERCURY HALIDE \(B^2\Sigma^+\) VIBRATIONAL DISTRIBUTIONS FROM DISSOCIATIVE EXCITATION REACTIONS OF Hg HALIDES WITH Xe\(^{3P_2}\) AND N\(_2\(A^2\Sigma^+_u\)\)


The HgX\((B^2\Sigma^+-X^2\Sigma^+)\), X = Cl, Br, I, spectra from the dissociative excitation reactions of N\(_2\(A^2\Sigma^+_u\), v = 0, 1) and Xe\(^{3P_2}\) with several mercureic and methylmercury halides have been simulated to assign the HgX(B) vibrational distributions. The distributions from the methylmercury halides could be described as Boltzmann types with temperatures ranging from 1000K for N\(_2\(A\) + CH\(_3\)HgI to 9000K for Xe\(^{3P_2}\) + CH\(_3\)HgCl. The distributions from the mercureic halides are non-Boltzmann and the \(<f_\nu>\) are somewhat higher than for the CH\(_3\)HgX compounds. The initial HgX(B) vibrational distributions are used to discuss the state-to-state quenching mechanisms.
4) A FLOWING AFTERGLOW STUDY OF THE QUenchING REACTIONS OF Hg($^3P_2$) AND Hg($^3P_0$) ATOMS BY HALOGENS, MIXED HALOGENS AND POLYATOMIC HALIDES


Mercury ($^3P_2$) and ($^3P_0$) metastable atoms were prepared in a flowing afterglow reactor by flowing He, Ne or Ar carrier gas containing Hg through a hollow-cathode discharge. The interaction of Hg($^3P_2$) with 30 halogen containing molecules was studied by observation of HgX(B), X = Cl, Br, and I emission; the intramultiplet relaxation to Hg($^3P_1$) also was monitored for some of the molecules, 5 diatomic molecules, NH$_3$, CH$_4$, and CF$_4$. By the addition of N$_2$ after the discharge, the Hg($^3P_2$) state can be removed and the reactions of Hg($^3P_0$) can be studied. The branching fraction for HgX(B) formation is much lower for Hg($^3P_0$) reactions than for Hg($^3P_2$) reactions. The HgX(B) emission spectra were obtained at sufficiently low pressure that vibrational relaxation is avoided and computer simulation of the spectra gives initial Hg(B) vibrational state distributions. A close similarity is found for the HgX(B) branching fractions and vibrational distributions with the analogous Xe($^3P_0$) atom reactions yielding XeCl(B,C) for halogens, mixed halogens, and ICN. The excitation transfer reaction between the Hg($^3P_0$) and CN also was observed. Upper limits are set for the bond energies of several nitrogen halides (CF$_3$NCl-Cl, CF$_3$NCl-Br, CF$_2$ClNCl-C1, CF$_2$ClNF-C1, CF$_2$N-C1).

5) VIBRATIONAL RELAXATION OF HgCl(B) AND HgBr(B) IN Ar AND Ne


A hollow-cathode, flowing afterglow apparatus was used to study the vibrational relaxation of HgCl(B) and HgBr(B) in a very high vibrational level with Ar and Ne bath gases. The bound-free emission spectra resulting from the reaction of Hg($^3P_2$) with various chlorine and bromine donors were recorded for 2-20 torr of Ar and Ne. These spectra were simulated to obtain HgCl(B) and HgBr(B) vibrational distributions vs. pressure. By using different Cl and Br donors, different ranges of vibrational energy were emphasized. An exponential gap model was used to characterize the V-T energy transfer from each collision. The collision cross-sections are large and near gas kinetic in magnitude. These results are qualitatively similar to those for vibrational relaxation of XeCl(B) by Ne and Ar.