VIBRATIONAL ENERGY TRANSFER AND KINETICS OF HIGH ENERGY MOLECULAR LASERS

FINAL REPORT, 1 Jun 76 - 31 May 79

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17 AUG 79

U. S. ARMY RESEARCH OFFICE

GRANT DAAG29-76-G-0252

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# Vibrational Energy Transfer and Kinetics of High Energy Molecular Lasers

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## Contract or Grant Number(s)
Grant No. DAAG29-76-C-0252

## Security Classification
Unclassified

## Distribution Statement (of this Report)
Approved for public release; distribution unlimited.

## Abstract
Vibrational energy transfer probabilities were measured for the H$_2$-D$_2$, H$_2$-HCl, HF-HCN, DF-HCN, and H$_2$-HCN systems from 220-450°K. Two-photon photodissociation of HgCl, HgBr, and HgI was observed to produce highly electronically excited Hg atoms. Franck-Condon factors and r-centroids were calculated for the B$_2^-$-X$_2^+$ systems of HgCl, HgBr, and HgI.
The research conducted under this grant was primarily concerned with the measurement of energy transfer probabilities, photodissociation characteristics, and spectroscopic properties of molecular systems of interest for the development of high energy lasers. A brief summary of the principal results of this work follows.

A. Vibrational energy transfer for $H_2-D_2$ and $H_2-HCl$ mixtures from 220 to 450°K.

The HCl molecule is of interest since it can be excited to produce vibrational laser transitions at wavelengths near 4 μ which are efficiently transmitted by the atmosphere. Evaluation of the possibility of an efficient $H_2-HCl$ transfer laser requires a knowledge of energy transfer probabilities in $H_2-HCl$ mixtures over a temperature range of interest for laser operation. A laser-induced fluorescence technique was employed for the measurement of $V \rightarrow V$ transfer rates in the $H_2-HCl$ and $H_2-D_2$ systems in the temperature range 220 to 450°K. The latter system is not of interest as a potential molecular laser candidate, but energy transfer in $H_2-D_2$ mixtures is of considerable fundamental interest in the development of theories for energy transfer.

Much attention has been given in the literature to vibrational and rotational energy transfer in hydrogen. An important reason for this interest is the existence of reliable potential energy surfaces for the $He-H_2$, $Li^+-H_2$, and $H_2-H_2$ systems. Full three-dimensional quantum calculations of vibrational and rotational energy transfer probabilities have been performed for these systems\(^1-4\) based upon recent progress in the approximate solution of the close coupled equations. These calculations have provided much insight concerning the influences on energy transfer of specific features of the interaction potential. Moreover, such important effects as the role of multiple quantum rotational inelasticity on vibrational deactivation processes have been described by the three-dimensional calculations.\(^1,2\)
Extensive experimental studies of vibrational relaxation in H₂ and D₂ and their mixtures with rare gases have been reported. The experimental techniques have been based on the use of either shock waves or laser Raman absorption for the excitation of H₂ or D₂. The progress of vibrational relaxation to the translational degrees of freedom has been observed with the laser-schlieren technique. This method does not monitor the vibrational energy directly, but rather the density changes associated with energy transfer to translation during V + T relaxation are observed.

In the present work the laser fluorescence technique was used for the direct observation of vibrational relaxation of H₂ in the presence of D₂ and HCl. The present technique is much simpler than the Raman-absorption laser-schlieren method and has the important advantage that the direct observation of changes in the vibrational energy of H₂ permits the study of V + V relaxation processes in mixtures of H₂ with other gases.

The well known rapid V + V transfer between HF and H₂ has been used here to permit the selective vibrational excitation of H₂ by trace amounts of HF excited by laser absorption. The subsequent relaxation of vibrational energy from the coupled HF and H₂ molecules was monitored by observation of the laser induced fluorescence of HF. A detailed discussion of our experimental measurements is contained in the paper "Vibrational Energy Transfer for H₂–D₂ and H₂–HCl Mixtures from 220–450 K," published in Chemical Physics Letters, 42, 58–63 (1976).


Measurements of probabilities for vibrational energy transfer were performed for the temperature range 240 to 450°K for HF–HCN and DF–HCN gas mixtures. Energy transfer probabilities in these mixtures were found to exhibit a strong inverse temperature dependence over this temperature range. Rate measurements were also given for vibrational energy transfer in H₂–HCN mixtures at 298°K. The results obtained suggest the feasibility of cw chemical laser operation in HF–H₂–HCN mixtures on the 3.85 μ HCN(001) + HCN(010) band.

Recently, vibrational energy transfer processes in gas mixtures containing the hydrogen halides HX (X=F, Cl, Br, I) have been extensively studied in the development of chemical lasers based upon HX reaction product
molecules. Energy transfer probabilities in such mixtures commonly exhibit a strong inverse temperature dependence below about 400°K. This dependence is associated with strongly anisotropic intermolecular potentials with minimum energy configurations that are favorable for vibration-to-vibration (V + V) and vibration-to-rotation (V + R) transfer.

Pulsed laser operation in the HCN molecule has been recently demonstrated. The highly polar HCN molecule, if regarded as a quasi-diatomic molecule, might be expected to exhibit energy transfer characteristics qualitatively similar to those of the HX molecules. Thus, the rapid rates and inverse temperature dependences for V + V, R energy transfer observed for many HX-gas mixtures should also be exhibited by similar mixtures containing HCN. However, the additional vibrational degrees of freedom for the HCN molecule provide some interesting differences between an HCN chemical laser and existing chemical lasers based upon HX molecules. The possibility of a cw HCN chemical laser based upon a complete population inversion on the HCN(001) + HCN(010) band at 3.85 µ makes studies of the flow of vibrational energy in HCN of considerable interest.

In the present work the V + V coupling of vibrationally excited HF, DF, and H2 to HCN has been examined to evaluate the feasibility of transfer-chemical-laser operation with HCN. Moreover, the use of either HF or DF chemical lasers to excite traces of HF or DF mixed with HCN provides a convenient means for the study of vibrational relaxation within the HCN molecule. Energy transfer probabilities were obtained for the HF-HCN and DF-HCN systems for the range 240 to 450°K; similar data were also taken for the H2-HCN system at 298°K. The results of our work were reported in the paper "Vibrational Energy Transfer in HF-HCN, DF-HCN, and H2-HCN Mixtures," published in the Journal of Chemical Physics, 66, 3189-3196 (1977).

C. Two photon excitation of mercury atoms by photodissociation of mercury halides.

Laser sources based on the (B²Σ-X²Σ) bands in HgCl, HgBr, and HgI are of considerable current interest. Laser output has been recently observed from HgBr(B²Σ) and HgI(B²Σ) molecules produced by the photodissociation of HgBr2 and HgI2 with the 193 nm ArF laser.

\[
hv + HgX_2 \rightarrow HgX(B^2Σ) + X \quad (1)\]
In research partially supported on this Grant we observed very strong fluorescence from highly excited Hg atoms produced in the photodissociation of HgCl$_2$, HgBr$_2$, and HgI$_2$ with an ArF laser. The origin of this fluorescence for the HgCl$_2$ case appears to be the two-photon dissociation process

$$2hv + \text{HgX}(X^2\Sigma) \rightarrow \text{Hg}^* + X$$  \hspace{1cm} (2)

The ground state HgCl($X^2\Sigma$) molecules are formed by the precursor process

$$hv + \text{HgCl}_2 \rightarrow \text{HgCl}(X^2\Sigma) + \text{Cl}$$  \hspace{1cm} (3)

In the HgI$_2$ and HgBr$_2$ cases process (1) followed by radiative decay,

$$\text{HgX}(B^2\Sigma) + \text{HgX}(X^2\Sigma) \rightarrow hv'$$  \hspace{1cm} (4)

can contribute to the formation of HgX($X^2\Sigma$) molecules.

The results of these experiments suggest that laser emission from atomic Hg analogous to that observed in the photodissociation of Hg$_2$ should be possible with use of mercuric halides. It seems possible that other metal halides and alkyl or carbonyl metal complexes may be suitable for photodissociation lasers; many of these compounds were successfully used in discharge pumped lasers in previously reported studies from our laboratory [M. S. Chou and T. A. Cool, J. Appl. Phys. 48, 1551 (1977)].

We have performed related experiments on the photodissociation of the lead halides, PbI$_2$ and PbCl$_2$. These experiments have led to photodissociation lasers on atomic Pb transitions at wavelengths of 3639, 3683, 4057, and 7229 Å; the laser transition at 3683 Å had not been previously observed in other lead lasers. This work will be reported in a paper to be submitted to Chemical Physics Letters by A. C. Erlandson, J. A. McGarvey, Jr., N. H. Cheung, and T. A. Cool.

D. Spectroscopic studies of HgCl, HgBr, and HgI photofragments.

The recent discovery of strong laser transitions (19–24) on the $B^2\Sigma-X^2\Sigma$ bands of HgCl, HgBr, and HgI has created new interest in the spectroscopy of these systems which had received little attention since the original studies of Wieland over thirty years ago. (25–27) A need exists, in particular, for Franck-Condon factors for the conversion of emission intensity data into vibronic population distributions. Moreover, the computational capability now exists (28) for ab initio calculations.
of the potential energy curves for these systems; a close comparison of theory and experiments is essential. For these reasons, calculations of Franck-Condon factors and r-centroids based on the band intensity estimates of Wieland (25027) were undertaken with the support of this Grant.

The computer program TRAPRB developed by Jarmain and McCallum (29) was used for the computations. This program constructs Rydberg-Klein-Rees (RKR) potential curves from the available spectroscopic data (vibronic term values and rotational constants). The spectroscopic input data are represented with a Klein-Dunham series which is used in the RKR potential calculation. The Schrodinger equation is solved numerically to provide vibronic wavefunctions, Franck-Condon factors and r-centroids. These calculations are presented in detail in the paper "Franck-Condon Factors and r-centroids for the B^2Π-X^2Σ Systems of HgCl, HgBr, and HgI," published in The Journal of Quantitative Spectroscopy and Radiative Transfer, 21, 397-432 (1979).
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