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OPTICALLY PUMPED LASER ACTION AND ENERGY TRANSFER IN POLYATOMIC--ETC(U)
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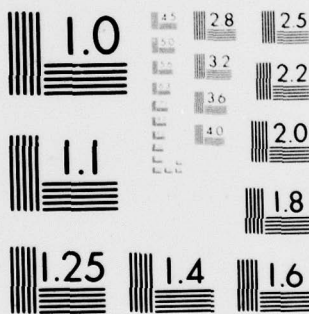
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Energy transfer and chemical decomposition processes have been studied in a number of molecules using laser fluorescence and time resolved thermal lensing techniques. Vibrational relaxation of OCS, vibrational energy exchange between isotopic species of CH₃F, and the laser driven, CH₃F sensitized decomposition of tetramethyl dioxetane have all been investigated

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The findings of this report are not to be construed as an official Department of the Navy position, unless so designated by other authorized documents.

List of Publications

1. Mode to Mode Energy Transfer in OCS Directly Pumped by a CO₂ Laser, D. R. Siebert and G. W. Flynn, J. Chem. Phys. 64, 4973 (1976)
2. Infrared Laser Double Resonance Study of Vibrational Energy Exchange between ¹²CH₃F and ¹³CH₃F, J. M. Preses and G. W. Flynn, J. Chem. Phys. 66, 3112 (1977)
3. Time Resolved Infrared Laser Photochemistry and Spectroscopy: The Methy Fluoride Sensitized Decomposition of Tetramethyl-1,2-dioxetane. An Example of Infrared Laser Induced Electronic Excitation, W. E. Farneth, G. W. Flynn, R. C. Slater, and N. J. Turro, J. Am. Chem. Soc. 98, 7877 (1976)
4. Translational and Vibrational Energy Distributions in Metastable Laser Pumped Polyatomic Molecules: A Quasithermodynamic Approach, Irwin Shamah and George Flynn, J. Chem. Phys. 69, 2474 (1978)
5. Vibrational Energy Transfer in CD₃F, L. A. Gamss, B. H. Kohn, A. M. Ronn, and G. W. Flynn, Chem. Phys. Lett. 41, 413 (1976)
6. Vibrational Steady States Produced by the Vibrational Relaxation of Laser Pumped Polyatomic Molecules, Irwin Shamah, Thesis, Columbia University, 1977.

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Introduction

Substantial progress has now been made in energy transfer studies involving small polyatomic molecules using laser fluorescence, double resonance, and thermal lensing techniques. We have described in detail these experimental methods as well as the basic principles which govern mode to mode energy transfer and molecule to molecule energy transfer¹. In addition we have published a massive review of laser applications to the study of molecular energy flow². This review describes much of the work which has been performed in the energy transfer field over a period of several years, a significant fraction of which has been carried out in our laboratory. In the following sections we summarize briefly work on individual molecules which has been performed under the present grant.

1. Mode to Mode Energy Transfer in OCS

Laser-induced fluorescence has been observed from all fundamental vibrational states in OCS.³ The fluorescence risetimes indicate rapid V-V energy transfer between the ν_2 and ν_3 modes, but suggest a considerably slower (by a factor of 7) V-V equilibration between the ν_1 and ν_2 modes. The $\nu_2 - \nu_3$ equilibration has been studied in OCS-rare gas mixtures. The results of these studies are consistent with a rate limiting filling of ν_3 from the level $4\nu_2$. Electrical anharmonicity of the ν_2 bending mode probably plays a major role in this transfer process. In particular, a long range dipole-dipole calculation for the probability of energy transfer between $4\nu_2$ and ν_3 is in very good agreement with the experimentally observed probability. Mechanical

anharmonic mixing of $4\nu_2$ and ν_3 appears to be too small to account entirely for the efficient bend-asymmetric stretch equilibration, though such mixing may play at least a small role in the energy transfer process. There is some evidence that, at least in the case of OCS-helium mixtures, several paths may contribute significantly to the equilibration of the ν_2 and ν_3 modes.

The ν_1 - ν_2 energy transfer rate is slow compared to the ν_2 - ν_3 rate but is consistent with existing evidence concerning comparable V-V processes in other triatomic molecules such as SO_2 and CO_2 . The slow equilibration of the ν_1 mode with ν_2 and ν_3 is, of course, consistent with the observation of laser action between ν_3 and ν_1 in an electric discharge.⁴ Presumably, the ν_3 mode temperature increases significantly due to electron-molecule collisions while ν_1 is only weakly coupled to both the electron temperature and to ν_3 . Very recently, laser action has been achieved in OCS on the $2\nu_2 + \nu_2$ transition after laser pumping the $0 \rightarrow 2\nu_2$ overtone with a T.E.A. CO_2 laser in a manner similar to the present experiments.⁵

The decay of fluorescence from each fundamental mode in OCS displays substantial heating and all three modes have the same deactivation rate constant. These results indicate that the entire vibrational manifold is deactivated through the lowest-lying state, the ν_2 bending fundamental. The dependence of this fluorescence decay in rare gas collision partners is in reasonable agreement with the results of calculations based upon SSH V + T theory. This agreement with V + T theory indicates that V + R relaxation

does not contribute appreciably to the deactivation of laser-excited OCS, in contrast to the results of similar experiments performed on CH_3F , CH_3Cl , CH_4 , and CD_4 . The calculated probability for V-T deactivation of the ν_2 mode in pure OCS is in excellent agreement with the observed V-T decay rate.

In general, the V-V rates in molecules composed of all heavy atoms appear to be 2-3 times slower than V-V rates in molecules containing light atoms provided comparable densities of vibrational states are considered.

In the present experiments the bending manifold of OCS can be assumed to be in equilibrium before bend-stretch equilibration occurs. Under these circumstances a variety of paths for bend-stretch equilibration can be expected to have comparable energy transfer probabilities. In principle, such paths can be distinguished by observing the dependence of the energy transfer rates on laser pump power since some paths involve excited state-excited state collision processes while others involve only excited state-ground state collision processes. Experiments are presently under way to test this point.

2. Vibrational Energy Exchange between $^{12}\text{CH}_3\text{F}$ and $^{13}\text{CH}_3\text{F}$

The infrared-infrared laser double resonance technique has been used to study vibration to translation (V-T) and vibration to vibration (V-V) relaxation behavior of several molecules such as CO_2 , SF_6 , BCl_3 , and C_2H_4 .⁶⁻¹¹ Double resonance experiments are complementary to fluorescence methods since double resonance can be used to study the relaxation behavior of vibrational levels which either fluoresce weakly or at a wavelength very near that

of the pump radiation, where small fluorescence signals may be obscured by relatively massive amounts of scattered pump radiation.

The V-V energy transfer rate from $^{12}\text{CH}_3\text{F}$ to $^{13}\text{CH}_3\text{F}$ has been measured using laser infrared-infrared double resonance.¹² The rate, in the exothermic direction, was found to be $1.5 \pm 0.3 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$. A symmetric top-symmetric top energy transfer calculation employing the long range dipole-dipole interaction using the methods of Sharma and Brau^{13,14} yields reasonable agreement with experiment. The observed $^{12}\text{CH}_3\text{F}$ - $^{13}\text{CH}_3\text{F}$ isotopic exchange rate is similar to the rate observed for ladder climbing excitation of the ν_3 mode in CH_3F which leads to excitation of the $2\nu_3$ and presumably $3\nu_3$ states after laser pumping of ν_3 . These results lend further evidence to the idea that collisions are largely responsible for rapidly populating high lying excited states near 3000 cm^{-1} in CH_3F after excitation of low lying states near 1000 cm^{-1} under our experimental conditions.

3. The Methyl Fluoride Sensitized Decomposition of Tetramethyl-1,2-dioxetane.

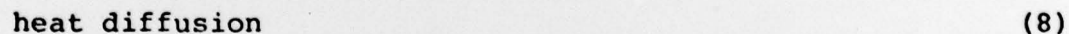
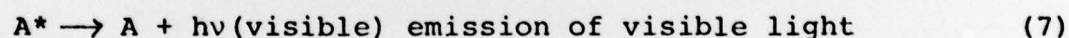
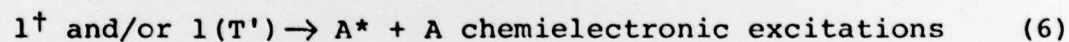
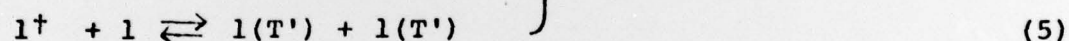
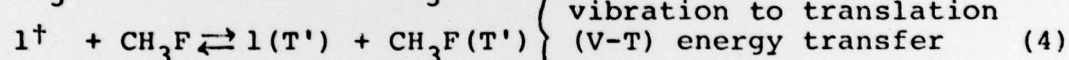
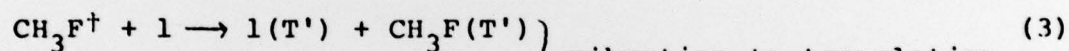
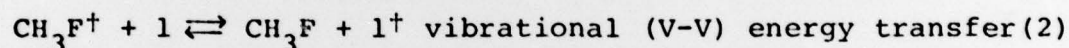
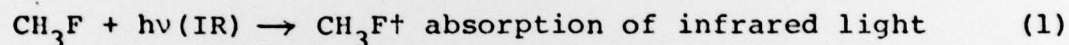
The enhancement of chemical reactivity by infrared light absorption has been demonstrated in a variety of systems.¹⁵ Efforts to date have fallen characteristically into one of two domains: (1) bimolecular reactions involving selectively excited small molecules (two, three atoms) in which the goal was to obtain detailed information on the dynamic course of the reaction,¹⁶ (2) bulk reaction studies in which product identities and yields have been used to demonstrate the potential of IR laser excitation for produc-

tion of unusual, or at least enhanced, chemical reactivity.¹⁷ The competition between collisional energy transfer processes and chemical reaction, which plays a crucial role in determining the mechanism of a laser initiated chemical reaction, can be probed using pulsed infrared excitation followed by time resolved detection of the reaction and energy transfer coordinates. We report here initial studies on a system that is capable of yielding this type of information, the pulsed CO₂ laser-enhanced decomposition of gas phase tetramethyl-1,2-dioxetane (1) in a methyl fluoride bath. Methyl fluoride is a "sensitizer" for the CO₂ laser induced decomposition of tetramethyl-1,2-dioxetane (1). Some unique features of this system are: (a) the observed infrared photochemistry is extremely clean, acetone being formed quantitatively; (b) the IR laser induced decomposition of (1) is accompanied by the emission of blue light ($\lambda_{\text{max}} \approx 410 \text{ nm}$); (c) the thermochemistry of (1) is well established and is such that acetone may be produced in an electronically excited states;¹⁸ (d) the reaction dynamics can be probed after excitation by monitoring time-resolved translational temperature changes (probed by the thermal lensing opto-acoustic technique);^{19,20} (e) energy transfer processes in CH₃F are well understood^{21,22} and serve as a benchmark for rate measurements in the mixture.

Irradiation of mixtures of CH₃F (2-30 Torr) and (1) (vapor pressure ≈ 1 Torr at 25°C) with an unfocused CO₂ TEA laser (1 μs pulse duration; 300 mJ per pulse) operating on the P₂₀ (9.6 μ) line is accompanied by blue luminescence from the reaction cell and results in a smooth conversion of (1) to acetone. Laser radiation at this frequency excites only CH₃F although the luminescence is observed

only when both CH_3F and (1) are present in the cell. Thus, CH_3F is a true photosensitizer.

In two other experiments using different experimental configurations the 3μ infrared emission emanating from the C-H stretches in CH_3F was monitored using the laser induced fluorescence technique, and the translational temperature rise was monitored using the thermal lensing technique. These experiments show clearly that reaction is initiated by IR absorption into CH_3F and that the visible light generated by decomposition of 1 is produced on an energy transfer timescale. The following mechanism serves as a model to explain these observations (A = acetone).



In this mechanism, daggers refer to vibrationally hot, translationally cold molecules and asterisks refer to electronically excited acetone, while T' refers to species whose translational temperature T' is above the ambient equilibrium temperature of the gas mixture. The thermal decomposition of 1 is known to be chemiluminescent due to the efficient formation of A*. According to our mechanism, the blue luminescence should therefore correspond to electronic emission of acetone. Indeed, the blue emission

produced by laser pumping was shown to be experimentally identical with acetone fluorescence.

In summary, this is the first example of an infrared photosensitized chemiluminescent organic reaction. A combination of measurements of infrared fluorescence from the photosensitizer, of visible luminescence from the primary product and of the translational temperature reequilibration are consistent with a predominant "temperature jump" mechanism (eq. 1-6) wherein any contribution from (1) in eq. 6 is dominated by the contribution from $1(T')$. These studies are being extended to 1,2-dioxetanes which directly absorb the laser pulse and to other systems in which a high energy content reaction possesses the potential of infrared laser induced electronic excitation.

4. Translational and Vibrational Energy Distributions in Metastable Laser Pumped Polyatomic Molecules.

A model is proposed to describe the vibrational steady state in a laser pumped polyatomic gas.²³ Such systems are shown to be characterized by a multiple temperature distribution with temperature relationships governed by the vibrational energy transfer pathway. In the harmonic oscillator limit each vibrational mode is at a single mode temperature, different from the translational/rotational temperature, leading to simple expressions for the steady state thermodynamic quantities. Additional constraint equations allow the complete determination of the temperature distribution and thermodynamic quantities in terms of two initial parameters, input energy and ambient temperature. Examples of multiple temperature distributions have been obtained for laser pumped CH_3F

undergoing various relaxation pathways and at a variety of initial conditions. The selection of the hottest vibrational mode was found to depend only on the path, and this mode may not necessarily be the one with the smallest energy spacing nor the one that is actually pumped. The extent of the vibrational enhancement of this mode is dependent on the initial conditions through the conservation equations. A stable multiple temperature condition was found to exist only if a restricted number of energy transfer paths are allowed.

5. Vibrational Energy Transfer in CD_3F

Infrared fluorescence from the ν_2 and ν_4 vibrational levels has been observed in CD_3F following excitation by a 10.6μ Q-switch CO_2 laser.²⁴ The exponential deactivation rate constant was found to be $0.44 \text{ msec}^{-1} \text{ torr}^{-1}$ for the pure gas. The rate constants for deactivation by the rare gases have also been measured and vary between 3.26 and $0.025 \text{ msec}^{-1} \text{ torr}^{-1}$. A lower limit of $500 \text{ msec}^{-1} \text{ torr}^{-1}$ was set on the ν_1, ν_4 activation rate.

The V-T/R deactivation rate constants are in general qualitative agreement with the results for similar molecules and particularly with those of the nondeuterated species, CH_3F .^{25,26} The CD_3F self deactivation rate constant, $0.44 \text{ msec}^{-1} \text{ torr}^{-1}$ is of the same order of magnitude as the $0.59 \text{ msec}^{-1} \text{ torr}^{-1}$ reported for CH_3F . The CD_3F -rare gas rate constants also behave as expected, decreasing with increasing mass of the collision partner except for an unexplained higher value for Xe. Again, save for the Xe case, the general trend of these results and even their

magnitudes are similar to those observed for CH_3F .

The vibrational energy transfer results obtained for CD_3F conform well to the pattern established by the results of previous studies on other members of the methyl halide and deuterated methyl halide series. The slow V-T/R relaxation is consistent with a molecule where at least 903 cm^{-1} of vibrational energy, the height of the lowest fundamental, must be transferred into translation and rotation. The comparisons made with V-T/R theory are clearly qualitative, but reasonable in terms of the trends and general rules which can be discerned among similar molecules.

Acknowledgement

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