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INFRARED LASER AND REACTION RATE STUDY.

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Compiled by:

C. G. CALLAN, JR. J. W. CHAMBERLAIN H. EETTERMAN
H. M. FOLEY P. L. KELLEY H. KILDAL D. C. LORENTS
R. NOVICK R. OSGOOD C. K. RHODES M. RUDERMAN
H. SCHLOSSBERG

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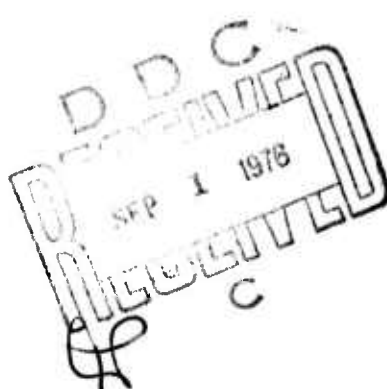
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PREFACE

The participating members of the 1975 JASON Winter Infrared Laser and Reaction Rate Study held from 6 to 10 January 1975 at SRI New York are as follows:

<u>Group Members</u>	<u>Affiliation</u>
D. Brabson	Air Force Weapons Laboratory
C. G. Callan, Jr.	Princeton University
J. W. Chamberlain	Rice University
H. M. Foley	Columbia University
P. L. Kelley	MIT Lincoln Laboratory
N. M. Kroll	University of California, San Diego
D. C. Lorents	Stanford Research Institute
R. Novick	Columbia University
R. Osgood	MIT Lincoln Laboratory
C. K. Rhodes*	Lawrence Livermore Laboratory
M. Ruderman	Columbia University
H. Schlossberg	Air Force Cambridge Research Laboratory

* Present address: Molecular Physics Center, Stanford Research Institute, Menlo Park, California 94025.

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I SUMMARY*

The main objective of this study was the determination of the areas that would have the greatest impact on the development and applications of infrared laser technology. This analysis is a companion to the previously published study^{1†} on visible and ultraviolet systems.

Since infrared laser development has an extensive history and has been developed on a national scale, it was anticipated that certain areas would merit expansion, but that others would not. As indicated below, and within the body of this report, this expectation was verified. The areas of major concern that deserve an expanded effort are vibrational energy flow, laser chemistry, and frequency conversion. On the other hand, the areas related to submillimeter waves, electronic-to-vibrational energy transfer, and electron excitation of molecules, although important, seem adequately supported at the current time and are not recommended for substantive expansion.

It is clear that infrared laser technology will have a large, and in many instances, unanticipated influence on defense issues, industrial development, and energy. It also appears to this committee that a properly structured effort can very effectively derive maximum advantage, at a fractional cost, from the enormous investment that has occurred in this field over the last decade. The utility of additional intelligently directed investment is high.

* This section was prepared by C. K. Rhodes.

† References are listed at the end of the report.

Detailed conclusions and recommendations pinpointing particular technical issues are presented in this report. The specific topics that need to be addressed, together with the recommended effort and priority, are given in Table 1. Priority 1 indicates that a substantial expansion is warranted, while Priority 2 is assigned if the current level of activity is regarded as adequate.

Table 1

RECOMMENDED ANNUAL RESEARCH EFFORT AND PRIORITIES

Technical Area	Priority	Additional Personnel	Report Section
Vibrational energy transfer processes	1	10	III-A
Selective vibrational excitation and chemical reactions	1	10	III-B
Optical pumping and nonlinear infrared processes	1	10	III-C
Far infrared and sub-millimeter radiation	2	0	III-D
Electronic-to-vibrational energy transfer processes	2	0-2	III-E
Electron excitation of molecules	2	0	III-F

The overall conclusions and recommendations of this study concerning the development and applications of infrared laser technology can be summarized as follows:

- (1) A properly structured program of about \$5 million per year directed at key technical areas can dramatically expand the utility of the infrared technology that has been established over the last ten years. This represents approximately 30 supported professionals, estimated at about \$3 million per year, with a capital budget of about \$2 million per year.
- (2) A variety of technical issues require additional research. These have been identified and are listed in Table 1 along with an assignment of priority and an estimate of the additional manpower required.
- (3) The time scale for substantive progress is estimated at three years. The length of this period reflects the relatively well developed state of this technology.

II INTRODUCTION*

In the 1974 JASON Summer Study on High-Energy Visible and Ultraviolet Lasers¹ the technical aspects that are central to the development of visible and ultraviolet systems were examined. On the basis of that study, a set of recommendations was formulated that indicated the research directions and priorities it is believed will have maximum impact on the development of a visible or ultraviolet system of high power and efficiency. On account of the wavelength regime considered, the conclusions of the 1974 Summer Study naturally concentrated on electronic properties and interactions and stressed, for example, the structure of electronically excited molecules,[†] electronic energy transfer,[†] and electronic chemiluminescence.[†] The common theme was the need to gain a more complete understanding, both analytically and experimentally, of electronically excited manifolds of atomic and molecular species.

The present study examines the corresponding issues in relation to systems that interact in the infrared spectral region, and in that sense may be properly regarded as a natural and complementary extension of the prior study to longer wavelengths. Since nuclear motions (vibrational and rotational) have characteristic frequencies throughout the infrared region, we anticipate that the behavior of the nuclear degrees of freedom will dominate this analysis as did the electronic motions in the previous

* This section was prepared by C. K. Rhodes.

† For the discussions of these areas the reader is referred to Section III-A of the 1974 Summer Study.¹

report. As high and low notes can blend to constitute an harmonious whole, these two reports combine to form a unified discussion of the full spectrum from $\sim 100 \mu\text{m}$ to $\sim 1000 \text{ \AA}$.

In contrast to this parallel development, however, an important difference exists between the visible and infrared spectral regions. This distinction arises mainly from the fact that large and high-average-power coherent sources currently exist for the latter, but not the former spectral range. Another distinction involves excitation mechanisms; thermal pumping is useful in the infrared, but inapplicable in the ultraviolet.

Table 2 presents the properties of the molecular systems that constitute the main sources of coherent energy in the infrared region. To a certain extent the situation expressed by Table 2 relaxes the need for the further development of independent primary sources of coherent radiation in this region. This fact represents an important flexibility not presently available in the visible range. Consequently, it is now useful to inquire about how the properties of this readily available infrared energy can be controlled, modulated, or used otherwise. In this context, for example, we would expect that processes enabling efficient frequency conversion would acquire considerable importance.

Finally, we note an interesting property of the entries to Table 2 concerning the available wavelengths. These frequencies are closely matched to (1) typical hydrogen vibrational modes ($\text{HF} \sim 3 \mu\text{m}$), (2) common CO, CN, NO, and NN modes ($\text{CO} \sim 5 \mu\text{m}$), and (3) a wide variety of other fundamentals (e.g., C-F) and molecular bending modes that are close to CO_2 at $10.6 \mu\text{m}$. This will facilitate the coupling of this energy to wide classes of molecular systems.

We observe that the development of high-power devices is normally associated with increases in the density of the medium as a natural consequence of coupling to the primary energy source at a greater rate. Since

higher densities generally imply increased collision rates, we wish to emphasize the role of collisional phenomena, particularly in the contexts in which they can be used to favorably channel the flow of energy or influence the radiative properties of the medium. An important example is clearly vibrational-vibrational (V-V) energy transfer between vibrational modes that partition the energy weakly in the kinetic degree of freedom. This stress on the details of collisional amplitudes is completely in the spirit of the previous 1974 Summer Study.

Table 2

INFRARED MOLECULAR LASER SYSTEMS

Property	CO ₂	CO	HF
Wavelength	10.6 μm	5 μ	2.7 μ (DF 3.8 μm)
Efficiency	~5% - 10%	~50%	3.3% chemical 180% electrical
Energy density	15 J/l (3 atm)	100 J/l (100 ton)	96 J/l
Small-signal gain	0.045 - 0.055 cm^{-1}	~0.10 cm^{-1}	Very high
Demonstrated energy output	200 J (1 ns)	200 J (100 μs)	2.3 kJ (35 ns) 0.8 kJ (6 ns)
Wavelength conversion	Demonstrated at low conversion	Not demonstrated	Not demonstrated
Average power	High (flow)	High (flow)	High (flow)

From a technical standpoint, this report formulates specific conclusions and recommendations concerning both theoretical and experimental areas that are judged to have the greatest potential impact on the development and uses of infrared laser systems. These recommendations include an assignment of priority along with an estimate of the manpower that would constitute a total program addressing these issues.

III TECHNICAL TOPICS

A. Vibrational Energy Transfer Processes V-V, V-T, and V-R*

This section examines the relationship of infrared lasers to vibrational-vibrational (V-V), vibrational-to-rotational (V-R), and vibrational-to-translational (V-T) energy transfer in gases. Because the great majority of infrared gas lasers (and certainly those of greatest practical importance) operate on vibrational-rotational levels, knowledge of V-V, V-R, and V-T rates is essential if one is to effectively model and understand existing lasers. These rates are important in both thermally and electrically excited systems. Further, with a tabulation of these rates, it would be possible to predict the success of a new gas laser candidate, either an electric discharge laser (EDL) or a gas dynamical laser (GDL), a priori. Conversely, the development of infrared laser technology has radically improved the extent and depth of our knowledge of vibrational relaxation processes in gases.^{2,3} This improvement, in turn, has direct importance in fields such as gas dynamics, laser-induced chemical reactions,⁴ photochemistry, and laser technology.⁵

1. Experimental Techniques

Prior to the discovery of the laser, experimental investigation on vibrational energy transfer remained in the rather static confines of acoustical (dispersion) and shock-tube measurements. These techniques were limited in nature and did not provide precise state-to-state energy transfer data.

* This section was prepared by R. Osgood and J. W. Chamberlain.

The first major improvement, made possible by the development of the laser, was the technique of laser-induced fluorescence (LIF).² In essence, this method relies on using the narrow linewidths of the laser to selectively excite various vibrational-rotational levels in a gas. The temporal behavior of these states can then be monitored through observation of their characteristic infrared fluorescence. It is this technique that has permitted the greatest wealth of vibrational relaxation data to be gathered.

Stimulated Raman scattering (SRS)^{3,6} has been used as a technique for studying states that are not connected to ground via a dipole allowed infrared transition. The time behavior of the Raman excited vibrational state is generally monitored by observing the heating of the gas (as V-T energy transfer occurs) via the phenomenon of thermal lensing.

Although many variations on and improvements of the above methods have been developed, a major limitation of even more widespread application has been the lack of convenient and sufficiently high-power tunable laser sources. For example, the current knowledge of vibrational energy flow in polyatomic molecules is limited essentially to the molecules that absorb the 9- μm and 10- μm bands of the CO_2 laser.³ Conversely, much detailed knowledge of the V-V and V-T kinetics of the hydrogen halide molecules has been gathered as a result of the series of hydrogen halide lasers operating on $v = 1 \rightarrow v = 0$, $v = 2 \rightarrow v = 1$, and $v = 3 \rightarrow v = 2$ transitions.³ Development of high-power tunable sources would eliminate this limitation and allow the excitation of an arbitrary state, thus extending enormously the applicability of the LIF and SRS techniques.

More recently, work on optical and microwave probing of the product states of molecular collision has been accomplished. This approach has been successful in observing the details of collisions involving velocity changing and rotational energy transfer,^{7,8} as well as the product states of chemically reactive collisions.⁹ In essence, this

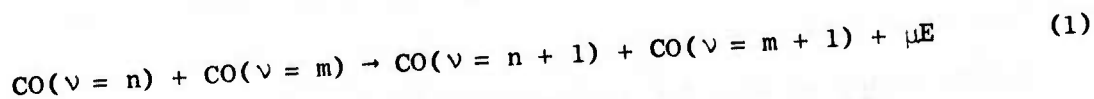
technique involves observing the absorption of a laser probe as a function of wavelength after the probe has passed through a cell containing the gas undergoing the particular collisional process. Such a technique obviously also requires a tunable laser, although of a different genre than the one mentioned above. Here the emphasis must be on stability and convenient tunability; laser power requirements are less stringent than in the case of LIF and SRS. Work on tunable IR sources such as laser diodes, the spin-flip Raman lasers, and nonlinear mixing¹⁰ has advanced to the point where limited experiments can be performed. However, much development must occur before these lasers become widely usable. In principle, it is possible to use visible lasers as probes; however, this avenue of approach has not yet been attempted for vibrational energy transfer. An alternative technique for probing the exit channels of vibrational energy transfer processes would be the molecular beam. Such an apparatus has the clear advantage of having the capability to measure both the differential cross section for the process and the individual product rotational states. These data are typically obscured in LIF experiments by the presence of molecular collisions. As will be discussed later, this capability is desirable for a definitive check on theories of molecular energy transfer. However, the cross sections of these processes are typically too small for obtaining an adequate signal-to-noise ratio (SNR) at a significant data rate. The main exceptions to this statement may be the cross section for V-V transfer in HF, DF, and other larger polyatomic molecules. Measurements of their HF cross sections in a molecular beam may be feasible.

2. Results of Measurements on V-V, V-T, and V-R Rates

The number of molecules and molecular rates studied by the above techniques is, nevertheless, imposing. For the sake of brevity we shall discuss only the following examples here: CO, the hydrogen halides, H₂, and polyatomic molecules in general. A more complete summary may be found in Ref. 3.

Because of the importance of the high-power CO laser, measurements of the rates of CO vibrational-energy transfer have been extensive. The exceptionally slow ($10^{-3} \text{ s}^{-1} \text{ torr}^{-1}$) vibrational-translation, rotation (V-T,R) time of the CO ($v = 1$) state in CO-CO collisions has been measured by SRS.¹¹ It is not clear whether this energy goes directly into rotation or translational energy or a combination of both. In spite of the large number of measurements, however, the corresponding V-T,R rates for $v = 2, 3, \dots, 20$ are not known. From a practical viewpoint, such data are necessary for accurate modeling of CO lasers. From a theoretical viewpoint, the variation of the V-T,R rate with v provides another comparison of theory and experiment.

V-V data for CO are, comparatively speaking, complete. Measurements of the process



where $m = 0$, and $n = 2 - 15$, have been made with both LIF,¹² chemiluminescence,¹³ and laser gain experiments.¹⁴ Such a series of measurements provides a superb opportunity for matching experiment with theory, and numerous attempts have been made.^{15,16} It would be desirable to have the analogous experiments for $m \neq 0$, just as it is desirable to measure the rates for excited vibrational states; the data would assist the practical problem of modeling and the academic problem of understanding.

Measurements of vibrational relaxation in the hydrogen halides has likewise been encouraged by laser development--in this case, by the development of chemical lasers. Extensive measurements at room temperature, via LIF along with shock-tube measurements at higher temperatures and the combined techniques at intermediate temperatures, have made the hydrogen halide systems the most thoroughly studied family of diatomic molecules in terms of vibrational energy transfer. As an example, Table 3 displays the array of measurements of the hydrogen halide V-T,R times. As

for CO, however, no definitive experiments exist that show whether the major part of the vibrational energy is lost directly to the rotational or translational channels. Table 4 gives a partial summary of the various V-V rates measured for the hydrogen halides. There are several measurements for processes involving the first and second vibrational levels. Data on the V-V rates for HF in $v = 3$ and $v = 4$, colliding with HF in $v = 0$ have also been obtained;¹⁷ however, the rapid V-T,R of HF has obscured interpretation. Thus, despite significant experimental accomplishments, knowledge of the dynamical behavior of the vibrational levels is far from complete.

Table 3

CROSS SECTIONS OF SELF-DEACTIVATION (V-T,R) OF VARIOUS
HYDROGEN AND DEUTERIUM HALIDE MOLECULES AT 300°K

Molecule	Vibrational State of Excited Molecule	Cross Section for Deactivation (normalized to the gas kinetic cross section)
HCl	1	1.3×10^{-4}
DCl	1	4.0×10^{-5}
HBr	1	1.2×10^{-4}
HI	1	7.0×10^{-5}
HF	1	8.0×10^{-3}
DF	1	3.8×10^{-3}

Although energy transfer in H_2 would appear to be the most interesting from a theoretical point of view, it has only recently received significant experimental attention. Because its vibrational modes are infrared-inactive, H_2 must be studied with SRS. This technique has not

yet been adapted to the investigation of V-V energy transfer, and the magnitude of the vibrational exchange cross sections for this important case of H_2 remain unknown. V-T data on H_2 have been measured for the regions from 77°K to 300°K with SRS and 1000°K to 3000°K with shock tubes. The low-temperature measurements indicate a factor of 2.5 difference in V-T self-relaxation of orthohydrogen and parahydrogen.¹⁸ The experimental situation with other simple homonuclear molecules is even more incomplete. For example, V-T data on both N_2 and O_2 have been collected only at room temperature and for temperatures greater than 1000°K. V-V data have not been measured for either molecule at any temperature. Homopolar diatomics are a particularly important class of molecules for laser applications, both as media for energy storage (N_2 and H_2) and as reactants in chemical lasers (H_2 , F_2 , Cl_2 , and Br_2). Therefore, a well-established set of V-V and V-T rates for these molecules is necessary for accurate modeling calculations of such lasers or chemically reacting systems.

Table 4
RATES (AT 300°K) FOR SEVERAL V-V EXCHANGE PROCESSES
INVOLVING HYDROGEN HALIDES

Collision Partner A	Collision Partner B	Energy Defect	Exothermic Rate (s ⁻¹ torr ⁻¹)
HF (v = 0)	HF (v = 0)	180	5.4×10^5
HBr (v = 2)	HBr (v = 0)	100	1.4×10^5
HCl (v = 2)	HCl (v = 0)	100	9.0×10^4
$H^{35}Cl$ (v = 1)	$H^{37}Cl$ (v = 0)	2	6.0×10^5
HCl (v = 1)	HBr (v = 0)	320	3.6×10^4
HCl (v = 1)	HI (v = 0)	650	5.4×10^3
HCl (v = 1)	DCI (v = 1)	800	3.3×10^3

Experimental measurements of vibrational energy flow in polyatomic molecules illustrate both the successes and the limitations of existing experimental techniques. The overall qualitative picture is clear. Intra- and intermolecular V-V exchange is rapid, with the exact magnitude of the rate depending largely on the degree of resonance of the collision. V-T,R rates are much slower because of their generally extreme nonresonant nature. While for many individual molecules several interesting features are reasonably well understood in a qualitative sense, a complete study of the vibrational energy transfer rates for any one polyatomic molecule does not exist.

A case in point is the linear triatomic species, CO_2 . Because of the existence of a well developed CO_2 laser technology, including stable piecewise-tunable devices and high-power CO_2 lasers, a multitude of experimental measurements have been made on CO_2 .³ These experiments include LIF, optical double resonance, and SRS. One result is that the vibrational energy transfer rate of the upper laser level (the asymmetric stretch mode) to other species is well established. In fact, the correlation of this rate with the energy defect of the transfer and the transition matrix elements of the transitions involved have yielded a valuable set of empirical selection rules for vibrational energy transfer.¹⁹ On the other hand, although "relaxation of the symmetric stretching and bending states of CO_2 (have) been exposed to much light,...the results have been (largely) unenlightening."²⁰ Of course, some data do exist on relaxation of these modes, and several general semi-quantitative facts are known. For example, one knows that the first excited state of the symmetric stretch mode relaxes rapidly, probably by equilibration with the bending-mode manifold. But the detailed structure of the energy flow is unclear. An interesting practical manifestation of this situation is the attempt to numerically model various forms of CO_2 lasers. In performing the modeling of the standard 10- μm CO_2 laser, the calculation is

relatively insensitive to many of the details of the energy flow through states other than those participating directly in the stimulated emission process. Thus, a knowledge of the type of semi-empirical facts mentioned above is sufficient to obtain a good fit with 10- μ m laser performance to the model, but is insufficient for other purposes. For example, an attempt was recently made to predict the success of a particular inversion mechanism for obtaining 16- μ m laser oscillation between two levels in the bending mode manifold of CO_2 .²¹ However, an accurate calculation could not be done because of lack of specific details about the kinetics of V-V and V-T transfer within and from that mode.

The situation is generally worse for other polyatomic species. Aside from a few particulars, the complete energy flow scheme is not known quantitatively. Undoubtedly, many of the rates can be measured if the available tunable IR laser technology is integrated into vibrational relaxation experiments.

3. Theory

In assessing the current theoretical understanding of vibrational energy transfer, it is appropriate to consider the following three foci of theoretical endeavor: V-T,R energy transfer, near-resonant V-V energy transfer and nonresonant energy transfer.

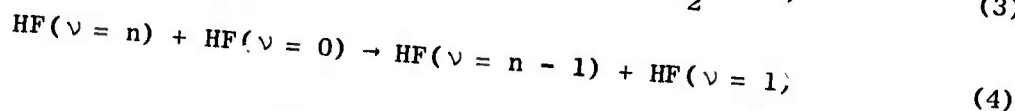
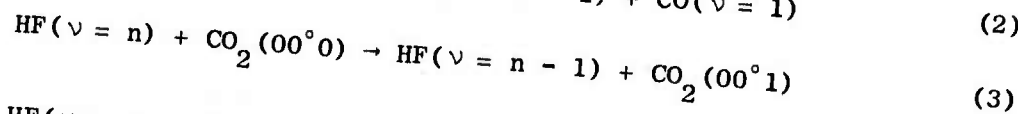
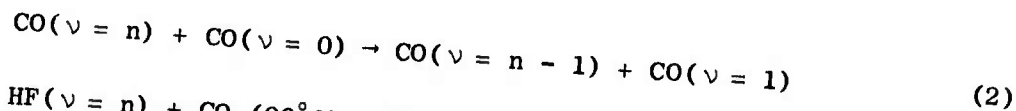
The most widely used theory of V-T energy transfer has been that of Schwartz, Slawsky, and Herzfeld (SSH).²² It uses the method of distorted waves and considers only the short-range repulsive case as the interaction potential. It ignores the rotational energy levels of the colliding molecule(s), and uses a "steric factor" to account for the lack of spherical symmetry in the molecular potential. The popularity of the theory may be attributed to its ability to predict the experimentally observed $(1/T)^{1/3}$ dependence (where T is gas kinetic temperature) of the probability of

deactivation per gas kinetic collision. It is also successful in predicting the approximate magnitude of this probability for collisions between "inert" molecules such as CO and N₂, and between these molecules and the rare gases. It is not successful in predicting either of these quantities if one or both of the collision partners is a hydrogen halide, or if the gas is at a temperature less than about 300°K. The failure is undoubtedly due to the fact that the theory does not take into account rotational energy levels and the attractive part of the intramolecular potential. Although several attempts have been made to include the above quantities in a revised theory, the results are not satisfactory.

The SSH theory has also been applied to the problem of resonant V-V transfer, where resonant is taken to mean an energy defect of less than about 1/10 of the mean translational energy. Unfortunately, the theory does not predict the observed 1/T temperature dependence of such transfer processes. An entirely different approach suggested by Mahan²³ and formulated in detail by Sharma and Brau²⁴ has been remarkably successful at predicting both the temperature dependence and the relative magnitude of resonant exchange probabilities. This theory uses a long-range multipolar interaction potential within the framework of the Born or distorted-wave Born approximation. It is therefore analogous to the pressure-broadening theories of Anderson and its later refinements. Unfortunately, the theory does not appear to be applicable to the case of HF-HF vibrational exchange and other collisions involving strong intermolecular potentials.

The problem of nonresonant V-V exchange is unique in that, of the three problems mentioned above, it offers the greatest number of experimental variables to be matched by theory. They are: relative magnitude of similar processes between like molecular species (e.g., HF-HF, HCl-HCl), temperature dependence of the cross section, and

variation of the cross section with vibrational number. The latter variable has been particularly well measured for the processes



and provides a variable unique to nonresonant V-V energy transfer. It is interesting that both the SSH and Sharma-Brau theories do not appear to fit experimental data. The SSH theory matches none of the experimental variables. The Sharma-Brau theory appears, at its current state of refinement, to predict rates that are too low by several orders of magnitude. Recently, Dillon and Stephenson¹⁶ have suggested an alternative approach that uses as a starting point the formal exponential scattering matrix, and considers both a multipolar and exponential interaction potential. The calculation is made tractable by an approximation that eliminates time-ordering from the exponential scattering matrix and by assuming a classical trajectory. Since the calculation preserves high-order processes, the relative magnitudes of multi-quantum (really multirotational quantum) processes are determined. The results show that for processes that involve vibrationally nonresonant collisions, but that have multi-quantum rotational transitions (which reduce the overall energy defect of the V-V transfer significantly), it is these rotational transitions that make the major contribution to the total cross section. The resulting calculations (at least for HF-CO₂ collisions) fit both the experimental absolute magnitude and the temperature and vibrational number dependence of the collisional cross sections. However, questions remain regarding the approximation that eliminates time-ordering and the choice of the interaction potential. Thus, an adequate theory cannot yet be considered an established fact.

In summary, of the three areas listed above, only the theory of near-resonant V-V energy transfer appears to be reasonably well understood. Furthermore, even this treatment seems questionable when dealing with collisions involving very strong and attractive intermolecular forces. Since a knowledge of all three of the above classes of collisions is important in laser engineering and related fields and since many important types of collision are not readily accessible to experimental measurement (for example, those involving certain excited states), it is important that theoretical understanding be sufficient that such rates be calculable.

4. Conclusions and Recommendations

The main conclusions and recommendations of this section are as follows:

- (1) V-V and V-T,R rates are important determinants of laser performance in either EDL or GDL configuration. Knowledge of these rates would enable a priori selection of new systems. Therefore, tunable laser technology can and should be applied to the measurement of vibrational transfer rates in a general fashion. With a few recent exceptions, all LIF and SRS measurements have been made within the limiting framework of fixed-frequency lasers. The use of tunable laser sources will result in a greater freedom to excite or probe any desired molecular or vibrational mode. Such a capability would not only greatly expand the catalog of known vibrational relaxation rates, but would also undoubtedly lead to a more thorough understanding of vibrational energy flow in important triatomic molecules like CO_2 and H_2O as well as larger systems such as NH_3 . The development of these sources is highly capital-intensive.
- (2) Measurements of V-V and V-T rates should be made for both collision partners in excited vibrational states (particularly in collisions involving CO and HF). These data are essential for accurate modeling of various forms of electrically and chemically excited molecular lasers and are important at high excitation densities. Existing theories are not sufficiently well tested that values calculated from them can be used with confidence.

- (3) V-V exchange data and the temperature dependence of V-T as well as V-V rates should be measured for H_2 and other homonuclear diatomic molecules. This information is useful both from a theoretical point of view (H_2 in particular) and from the vantage point of understanding laser devices that use N_2 and H_2 as energy storage molecules.
- (4) Vibrational transfer data on polyatomic molecules are fragmentary. Continued LIF, SRS, or other forms of experiments are necessary.
- (5) Efforts to improve the theories of V-T, R, and non-resonant V-V transfer should be supported. In the absence of a complete (omnimolecular) set of experimental data, theory provides the only means of estimating unknown rates. The above two classes of vibrational energy transfer, in particular, are not well understood.
- (6) An effort of approximately 10 scientists (supported) distributed to cover Items 1 through 5 above is recommended.

B. Selective Vibrational Excitation and Chemical Reactions*

Infrared lasers are producing a large and expanding impact on the study of gas-phase reactive systems. This arises from the possibility of preparing chemical reactants, in particular molecular vibrational-rotational states, and from the ability to measure precisely the intermediate and final states of both reactants and products. This has opened up the possibility of enormous growth in fundamental understanding and control of the detailed history of state-to-state chemical reactions in simple as well as complex systems.

* This section was prepared by C. G. Callan, Jr., M. Ruderman, and C. K. Rhodes.

Diverse phenomena have been observed to contribute to the chemical reactivity of molecular systems. Reactions have been driven by (1) thermal processes,⁴ (2) selective vibrational excitation,⁴ and (3) radiatively nonlinear unimolecular processes.²⁵ Aside from the demonstrated application to isotope separation, it is not yet obvious where the main impact of this broadly applicable technology will be. Nevertheless, it would be surprising if new and presently unexpected possibilities do not develop. The potential from fundamental research in this area appears very great relative to its present cost. Revolutionary advances appear probable.

In the discussion given below we examine several issues including (1) current activity, (2) status of research, (3) possible applications, (4) chemical reactions as a source of vibrational excitation, and (5) the significance of further fundamental data. A final subsection presenting conclusions and recommendations closes this analysis.

1. Current Activity

a. University Research

The initial enthusiasm in university chemistry departments for exploring the chemistry of selectively vibrationally excited molecules has been tempered by practical factors involving the limited wavelengths of available IR lasers and especially by the very limited accessibility of sophisticated laser and modulation devices. University funds are sufficient for the support of the involved scientists through faculty salaries and government grants for research associates. The latter are generally widely distributed small grants (~\$25,000). However, there are insufficient funds for new capital equipment, which has now escalated to \$25,000 to \$75,000, a very expensive range in terms of historic expenses for chemical research. Much research time and support is presently used in

constructing equipment that still does not equal commercially available equipment. There exist fewer than a dozen active, productive principal investigators distributed among half a dozen universities. Because of the widespread enthusiasm the number would be expected to increase markedly if the necessary lasers were more widely available.

b. Government Laboratories and other Non-University Research Institutes

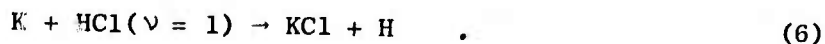
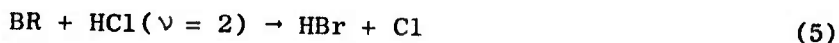
The evidence is that research in reaction chemistry has been limited in support. Some of the main large laboratories involved in laser development do not have any commitment to fundamental gas-phase chemical reactions for which these lasers are now the major and necessary research tool. It is an area that seems remarkably undersupported.

2. Status of Research

Experiments have mainly attempted to demonstrate that selective excitation of vibrational levels in a reaction can increase reaction rates. Somewhat less effort has gone toward an examination of the influence of reactant vibrational energy on the distribution of states in the product species. As noted in Section III-A, particular experiments have been restricted by the limited practical availability of appropriate IR lasers, so that no general program of exploration leading to a correspondingly deeper understanding has yet been possible. Advances in frequency conversion and the generation of tunable coherent energy throughout the infrared will naturally have a strong influence on this general capability (for these aspects the reader is referred to Section III-C).

Experiments in the gas phase generally are accompanied with nonspecific energy transfer by V-V and V-T mechanisms that diffuse the excitation energy into a large number of modes. This aspect often makes

it difficult to differentiate between the effect of selective vibrational excitation on reaction rates and general local heating of all degrees of freedom. Experiments reporting chemical reactions with selected vibrationally excited molecules include the following:^{3,4}



The rates^{26,27} of Processes (5) and (6) were increased by factors of 10^2 and 10^{11} , respectively, over the rate associated with vibrational ground state $\text{HCl}(\nu = 0)$. The latter process was useful in separating the chlorine isotopes ^{35}Cl and ^{37}Cl . Both of these experiments were possible because the reactant HCl is one of the currently available infrared sources. Indeed, in the molecular-beam-experiment²⁶ examining process (5), it was necessary to have the laser radiation match the $\nu = 0 \rightarrow \nu = 1$ transition frequency to within 50 MHz.

Excitation of higher bending modes of O_3 in the process^{28,29}

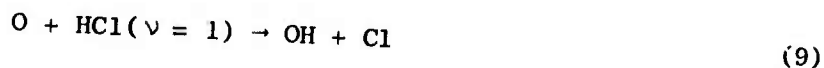


by CO_2 9.6- μm radiation increased the reaction rate by a factor of about 20, but vibrational excitation of NO did not exhibit a corresponding influence. This is interesting, since the NO vibrational quantum is approximately twice that of the quantum used to excite the O_3 mode. This behavior indicates the role of some subtle aspect of the reaction surface that is not determined solely by total internal energy content.

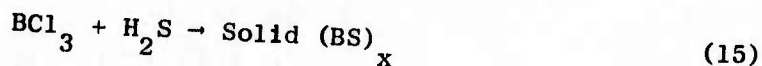
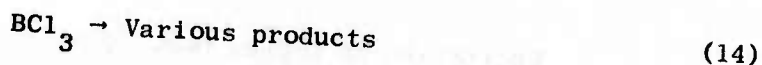
Excitation of the O_3 vibration in the reaction³⁰



produced a reaction rate increased by a factor of approximately three.
In addition, the rate for the process³¹



is reported to be $\sim 10^4$ greater for the vibrationally excited $\text{HCl}(\nu = 1)$ than for ground-state $\text{HCl}(\nu = 0)$ species. Other demonstrations of increased reaction rates arising from vibrationally excited reactants include:^{32,33,34}



Finally we note that multiple quantum processes leading to dissociative pathways, sometimes under even collisionless conditions, have been reported in several isotopically selective experiments.^{35,36,37} The materials include BCl_3 , SF_6 , and OsO_4 . An estimate of this type of behavior and its ramifications has been given previously.¹ Multiple quantum processes that coherently combine collisional and optical electric fields can also be expected to play an important role.³⁸

Selective vibrational excitation has currently been demonstrated to increase chemical reaction rates, often in a dramatic fashion. In many

cases it is much more effective than a similar increase in relative translational energy between reactants, but no general conclusion or understanding is yet possible even for the relatively simple systems so far studied. Effects from excitation and containment of energy in a single mode of more complicated polyatomics has not been explored at all. Even the transfer of energy between internal modes of polyatomics has been examined in fewer than a half a dozen cases. A substantial amount of intelligent experimental work will have to be done before theoretical understanding and predictability of the effect of vibrational excitation on chemistry is achieved. This appears to be one of the main dividends to be expected in the near term from continued research.

3. Possible Applications of Selective Vibrational Excitation

There is a known and demonstrated capability for isotope separation in certain reactions that may be very significant in processes for the separation of deuterium and uranium isotopes. But the present market for other isotopes in the U.S. is only $\$5 \times 10^6$ /yr. There may, however, be new demands for certain isotopes if vibrationally selected reactants can give a cheap source. Suggestions include:

- (1) Cheap abundant metal isotopes for diffusion studies that could have an important beneficial effect on the direction of metallurgical studies.
- (2) Agricultural experiments using cheap bulk fixed nitrogen isotopes and other isotopes in which plants can be grown.
- (3) Separation of rare earths O_2 and Hf, which may be competitive with other techniques.
- (4) Materials processing and polymerization.

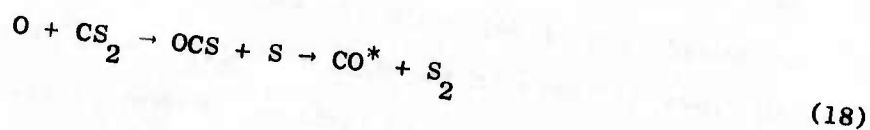
4. Chemical Reactions as a Source of Vibrational Excitation

The converse of the proposition that chemical reaction rates can be dramatically increased by vibrationally exciting the reactants is

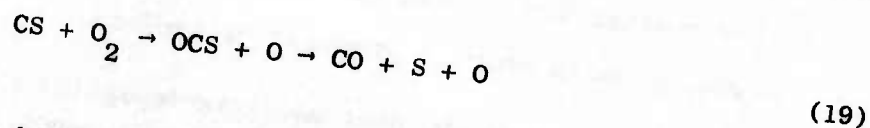
that the products of exothermic reactions will usually be preferentially produced in vibrationally excited states. If the vibrational-level distribution is naturally inverted, one would then have a simple pump mechanism for infrared lasers. This is a well established fact for the HF, DF, and CO chemical lasers. The basic pump mechanism of the HF laser utilizes the reactions



and produces HF molecules in highly excited vibrational states. This natural inversion is then used to feed laser action on one of the $\Delta v = 1$ vibrational transitions. Possible CO chemical lasers are based on



or



A similar process has been proposed by Polanyi³⁹ using

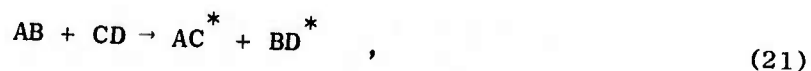


where X is a metal atom and AB is some gaseous oxidizer (e.g., O_2 and F_2). A chemical laser using $\text{Na} + \text{N}_2\text{O}$ in the presence of CO has been observed by Benson and Barger⁴⁰ to give $10.8 \mu\text{m}$ coherent radiation from N_2O .

Experimental work by Rice,⁴¹ who produced metal vapor by an exploding-wire technique, gives strong evidence for infrared laser

action, although it is not clear that the population inversion occurs by the simple direct path shown above.

In the above examples two problems occur. First, it is not trivial to produce the atomic reactant, X. Second, the vibrational inversion can be rapidly destroyed by collisions, probably limiting applications to the gas phase. This problem is of course common to all infrared lasers. As to the first problem, there is no apparent need to limit one's attention to metal and diatomic reactions. Any exothermic rearrangement collision, such as



would appear to be a good candidate for this type of laser, although no specific realizations of such a system exist.

It is perhaps surprising that more such potential laser systems are not known. To evaluate the potential of a particular reaction, one needs either to measure or compute the state-to-state reaction cross sections. Presumably, the new lines of chemical research discussed elsewhere in this report will lead to an accumulation of experimental information on this subject that will permit more fruitful speculation.

5. Significance of Further Understanding of Chemistry of Vibrationally Excited Molecules

The ultimate consequences of a deeper understanding of the mechanisms of chemical reactions are unpredictable, although certainly extensive. Serendipity rather than foresight might, as usual, be crucial in many cases. Vibrationally excited reactants affect reaction rates and the distribution of product channels. Moreover, excited products are often the intermediates for further reactions even when they do not produce directly observable consequences, as in IR lasers. Nevertheless, we list below some expected or conceived applications:

- (1) Upper-atmosphere chemistry. In this application initial reactants and product molecules that react further are usually vibrationally excited. For example, the crucial exothermic reaction $O^+ + N_2 \rightarrow N + NO^+$ has a low activation energy and is very sensitive⁴² to the vibrational excitation state of N_2 .
- (2) Rocket engines. Creation of low-temperature high-velocity beams. Here the flow of energy in combustion reactions, into and out of vibrational states, and ultimately into directed translational energy, needs to be understood in detail.
- (3) New chemical products. For this application it would be necessary to use vibrational state selection to help make expensive pharmaceutical type molecules by a less costly process. These are very complicated molecules and at present there is no basic understanding of ways of accomplishing this.
- (4) Fine tuning or control of chemical processes. This is certainly an intriguing prospect, but there are no important concrete proposals.

6. Conclusions and Recommendations

The main conclusions and recommendations pertaining to this section are as follows:

- (1) Control of reaction pathways through laser excitation of molecular vibrations is an area rich both in fundamental issues of reaction mechanisms and in future applications. Revolutionary results in this field are probable. The data currently available, although raw and empirical, are sufficient to establish the importance and promise of this field.⁴³ It is clear that further work of both an experimental and theoretical nature is justified and necessary to explore the full potential of the field.

- (2) Specific data on state-to-state reactive amplitudes of vibrationally excited polyatomics are, with minor exceptions, nonexistent. No case of highly excited vibrational modes is known, although we anticipate that these highly excited vibrational manifolds will dominate the reactive dynamics of a large class of laser-driven chemical processes including those of an isotopically selective character. Endothermic reactions fall naturally into this group.
- (3) For maximum impact, future studies should emphasize the mechanisms of reactive amplitudes and their relation to reactant and product vibrational energy. An important aspect of the analysis of these mechanisms is an understanding of how the order of the laser field can be translated into ordered reactions, and hence, ordered product systems. For this, all the degrees of freedom (amplitude, polarization, frequency, and spatial coherence) of the vector field should be utilized.
- (4) Mechanisms of nonlinear radiative coupling need emphasis. For this, detailed spectroscopic measurements are needed, with special attention accorded to perturbed spectra because they provide additional pathways for radiative coupling, particularly for states highly excited vibrationally and/or rotationally. Combined collisional and radiative coupling³⁸ will also be important.
- (5) An effort of approximately 10 scientists (supported) distributed to cover Items 1 through 4 above is recommended.

C. Optical Pumping and Nonlinear Infrared Processes in Gases^{*}

There are a number of well developed infrared gas lasers, most notably CO₂, CO, HF, and DF. Applications, particularly to photochemistry, often require infrared radiation of a precise wavelength, not available from one of these well developed lasers. The question naturally arises, therefore, whether there are techniques that can efficiently shift the wavelength of an infrared gas laser.

The field of nonlinear optics in crystals has been long investigated, and the techniques of harmonic generation, difference-frequency generation, and parametric oscillation are understood and available. Further development of nonlinear crystals is desirable, particularly for shorter wavelengths. However, these means of frequency conversion are often limited by the power-handling (average and peak) capability of available crystals with appropriate optical characteristics. Spin-flip Raman lasers, which require a high degree of technical sophistication, are available that produce watts of CW power in the 5-to-6.5- μ m region. Semiconductor diode lasers, which are only recently becoming commercially available in quantity, are capable of producing tens of milliwatts CW in the 4-to-25- μ m region. The diodes have been proven to be excellent for high-resolution spectroscopy, although their high cost (about \$3500) coupled with a somewhat limited tuning range and availability has tended to restrict the number of workers using these lasers. There is no question that solid-state devices will play an important role in infrared spectroscopy and, as such, they deserve to be encouraged; however, further discussion of these devices is beyond the scope of the present study.

^{*}This section was prepared by P. L. Kelley, H. R. Schlossberg, and C. K. Rhodes.

This section deals with several promising techniques involving molecular gases that have been demonstrated or analytically shown feasible. The techniques include optically pumped molecular lasers, with or without vibrational energy transfer, or near-resonant nonlinear optical processes such as stimulated Raman scattering, or four-photon parametric processes.

1. Optically Pumped Infrared Lasers

An optically pumped infrared laser uses an external laser to selectively populate (pump) a vibrational state in a molecular gas. The laser operates between the pumped state and a lower vibrational state connected by a nonvanishing transition moment that need not be allowed in the harmonic approximation. The upper vibrational state can be pumped directly by the external laser or by means of a selective vibrational energy transfer with another molecule directly pumped by the external laser. The direct pumping can be by means of single or multiple photon absorption, or other nonlinear processes such as stimulated Raman scattering.

a. One-Photon Pumping

The first demonstration of an optically pumped vibrational laser was by Chang and Wood⁴⁴ in 1972. They selectively pumped $00^{\circ}1$ state of CO_2 by means of its strong absorption at $4.3\text{ }\mu\text{m}$. The $4.3\text{-}\mu\text{m}$ radiation was from an external HBr laser. The CO_2 oscillated on the familiar $00^{\circ}1\text{-}10^{\circ}0$ transition at $10.6\text{ }\mu\text{m}$.

More recently, Schlossberg and Fetterman⁴⁵ used the $9.5\text{-}\mu\text{m}$ output from a CO_2 laser to pump the $\nu = 2$ level of the bending (ν_2) mode in OCS via a direct overtone absorption. Oscillation took place between $\nu = 2$ and $\nu = 1$ of the bending mode at $19\text{ }\mu\text{m}$. This work was important because it was the first demonstration of oscillation by optical pumping

with operation on a vibrational transition not previously observed in a discharge, and because it showed that pumping and subsequent oscillation could take place more rapidly than deleterious relaxation effects. Therefore, the OCS work shows the potential generality of optical pumping as a means for generating new wavelengths from existing lasers.

Theoretical aspects of direct optical pumping have been considered by Golger and Letokhov.⁴⁶ In a case where the rotational relaxation time is much less than the pump-laser pulse time, which is correspondingly much less than the vibrational (V-V) relaxation time (a case easily achieved with addition of rare gas), Golger and Letokhov show that saturation of the pumped vibrational level is achieved if the pump energy density E_p satisfies

$$E_p \gg \frac{\hbar\omega_p}{\sigma_{rr'}(f_{r'} + f_r g_{r'}/g_r)} \quad (22)$$

where $\hbar\omega_p$ is the pump photon energy; $\sigma_{rr'}$ is the cross section for the pump transition, with r and r' the rotational level of the lower and upper vibrational states respectively; and f_r and $f_{r'}$ are the fractional population of their respective vibrational states associated with r and r' and g_r and $g_{r'}$, which are the degeneracies of the r and r' states. If saturation is reached, then the population, N_u , in the upper level is

$$N_u = \frac{N}{1 + \frac{g_r f_{r'}}{g_{r'} f_r}} \quad (23)$$

with N the total number of molecules originally in both vibrational states (i.e., very nearly in the ground state). Since $g_r \sim g_{r'}$ and $f_r \sim f_{r'}$,

approximately half the ground-state molecules can be excited. To estimate Condition (22), consider a 10- μ m pump laser, and note that $f_{r \rightarrow r'} \sigma_{rr'} \approx \alpha_r / N$ where α_r is the linear-absorption coefficient for the transition $r \rightarrow r'$. For a typical transition in a polyatomic molecule, $\alpha_r \sim 0.01/\text{cm torr}$, which gives $E_p \gg 30 \text{ mJ/cm}^2$, a very nominal value. Thus, it is relatively easy to pump half of the ground-state molecules to an upper vibrational state. Whether this is sufficient for oscillation depends on the strength of the dipole matrix element to a lower vibrational level. In many cases the dipole moment between vibrational states not coupled in the harmonic oscillator approximation is on the order of 0.01 D, for which oscillation should be possible. It is particularly advantageous if the pumped level has a Fermi resonance with a vibrational level that is connected to the lower level of interest by a dipole moment in harmonic approximation.

If the dipole moment is known, the gain can be calculated, and the necessary length l for oscillation ascertained. The absorption of pump energy density is given by

$$\frac{dE_p}{dz} = N_u h\nu_p$$

or

$$E_p(0) - E_p(l) = N_u h\nu_p l \quad (24)$$

Condition (22) on $E_p(l)$ and Eq. (24) then determine the necessary input energy $E_p(0)$.

The above argument shows that it is extremely advantageous to have available integrated absorption data on hot bands of molecules of interest, from which dipole moment matrix elements can be calculated. There are few data of this nature available today.

b. Optical Pumping with Energy Transfer

An alternative to oscillation directly from an optically pumped vibrational state is to arrange for energy transfer to other vibrational states of the same molecule or another molecule. This vibrational energy transfer can result in population inversion if it is sufficiently selective. Alternatively, a vibrational equilibrium can be established at an effective temperature sufficiently higher than the rotational/translational temperature so that laser oscillation can occur between vibrational states on P transitions. An interesting possibility is the generation of wavelengths shorter than the pump wavelength by oscillation from a state higher than the pumped one. In this case energy transfer collisions in effect convert several input photons into one output photon. The importance of an understanding of vibrational energy transfer in making such lasers is obvious. This is discussed in Section III-A.

An optically pumped laser based on energy transfer was first demonstrated by Chang and Wood.⁴⁷ An HBr laser pumped CO_2 to the 00^0_1 state, which transferred to the 00^0_1 state of N_2O , which then oscillated to the 10^0_0 state. Several other cases have been demonstrated by Deutsch and Kildal⁴⁸ using a doubled CO_2 laser output as the pump. Oscillation has been obtained by this method in CO_2 , OCS , CS_2 , and N_2O by collisional energy transfer from optically pumped CO .

c. Two-Photon Pumping

Recently several efforts have shown the potential of two-photon optical pumping techniques. A general analysis by Kelley, Kildal, and Schlossberg⁴⁹ showed that near-intermediate resonant two-photon absorption of oppositely traveling beams can efficiently populate excited vibrational states. Experimental work by Bischel, Kelly, and Rhodes⁵⁰ on

CH_3F confirms this finding. In unpublished work, Fetterman has generated 16- μm laser radiation by optical pumping SF_6 with a CO_2 laser. The most reasonable explanation for the observed characteristics of this system involves two-photon pumping of the SF_6 molecules. A schematic of this process is shown in Figure 1. Here ω , ω_v , ω_v' , and ω_v'' are vibration-rotation frequencies, ω_L and ω_L' are the pumping frequencies, and ω is the output laser frequency.

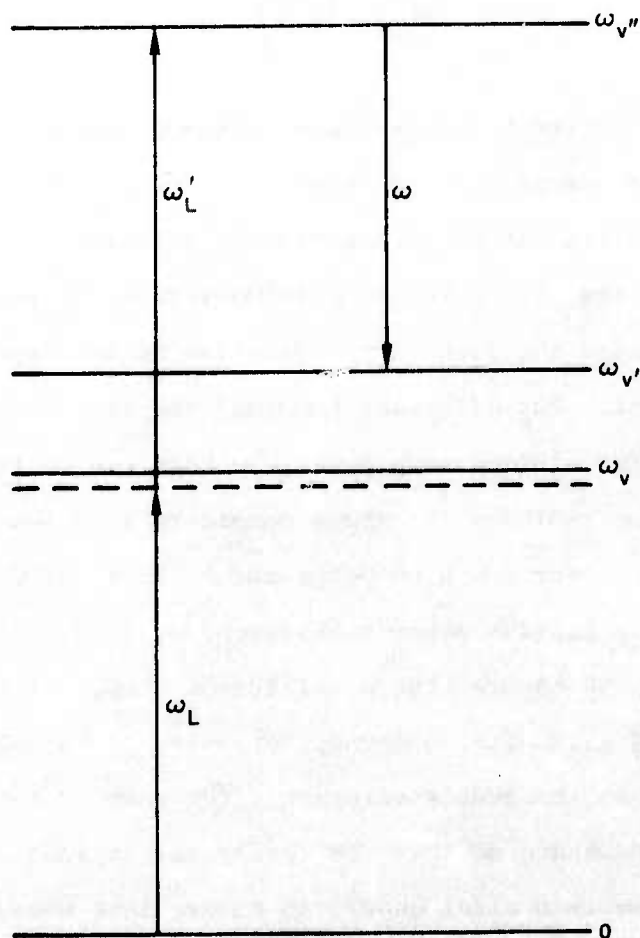


FIGURE 1 ENERGY-LEVEL DIAGRAM ILLUSTRATING TWO-PHOTON OPTICAL PUMPING. The symbols 0 , ω_v , ω_v' , and ω_v'' designate the vibrational-rotational frequencies of the molecular system while ω_L and ω_L' are the excitation frequencies and ω is the output laser frequency.

The work of Kelley et al.⁴⁹ showed that two-photon absorption is not feasible for infrared pump photons unless there is an intermediate level nearly resonant with one of the two pump frequencies.* For two visible pump photons, an intermediate level is not necessary, but is still extremely helpful. The nonlinear absorption coefficient can be enhanced by combining the two input photons in opposite directions. The nonlinear absorption coefficient is then given approximately by

$$\alpha_{NL} \approx \alpha \left(\frac{\mu E}{\hbar \delta \omega} \right)^2 \frac{\Delta \omega_L}{\gamma} \quad (25)$$

where E is the electric field strength (assumed comparable for the two inputs); μ is the infrared dipole moment; γ and $\Delta \omega_L$ are the homogeneous and inhomogeneous linewidths, respectively; α is the linear absorption coefficient of a transition to the intermediate state reckoned at exact resonance; and $\delta \omega$ is the frequency separation of one input field from the intermediate level. For efficient pumping, the length pumped, l , should be $\sim 1/\alpha_{NL}$, and for minimum pump power the beam can be focused to a radius $a \sim \sqrt{\lambda l}$. Equation (25) and the above considerations lead to an input power requirement. For $\mu \sim 0.06$ Debye and $\delta \omega/2\pi = 10$ GHz, Kelley et al.⁴⁹ have estimated the minimum power requirement at 1 kW. It is still, of course, necessary to ensure that a sufficient number of molecules are pumped to achieve gain after pumping. Further, if the desired wavelength is much longer than the pump wavelengths, the beam at the pump wavelengths will have to be expanded so that the former has an adequate Fresnel number. The above estimate is nominal enough to ensure that these effects can be

* For two-photon absorption, the two input frequencies could, of course, be the same--i.e., one input.

managed. The use of a waveguide for confinement could aid greatly. Two-photon absorption pumping offers the possibility of using a single pump laser to generate shorter-wavelength output.

We now estimate the gain for a down-conversion process to 16 μm for two cases, CH_3F and NH_3 , pumped by two-photon absorption of CO_2 radiation. The transitions^{50,51} of interest are illustrated in Figures 2 and 3. For this calculation, we assume a working pressure of ~ 10 torr and do not require cancellation of the Doppler effect in the pumping process. Calculating the vibrational and rotational partition functions for CH_3F and NH_3 , we conclude that the ground-state population in the $J = 2, K = 1$ rotational level of CH_3F is $2 \times 10^{14} \text{ cm}^{-3}$ while the corresponding value for the $J = 5, K = 4$ state of NH_3 is $\sim 4.8 \times 10^{14} \text{ cm}^{-3}$. If we saturate the two-photon transition, we can expect to put one-fourth of the CH_3F molecules and one-tenth of the NH_3 molecules into the upper laser level. A lower fractional population is assumed for NH_3 on account of the need for collisional inversion relaxation ($2^- \rightarrow 2^+$) in order to populate the desired upper 2^+ state. Both of these systems have transitions in the 16- μm range; these are the $2\nu_3 \rightarrow \nu_5$ and $2^+ \rightarrow 1^-$ transitions for $^{12}\text{CH}_3\text{F}$ and $^{14}\text{NH}_3$, respectively. Hence, the population differences ΔN for the CH_3F and NH_3 cases are $3 \times 10^{13} \text{ cm}^{-3}$ and $4.8 \times 10^{13} \text{ cm}^{-3}$, respectively.

The gain coefficient g for the 16- μm transition is

$$g = \frac{\lambda^2 \Delta N}{8\pi \nu c \tau_r} \quad (26)$$

where τ_r is the radiative lifetime of the 16- μm transition. The broadening parameters^{52,53} are nearly identical for the two cases and give a linewidth $\gamma \approx 7 \times 10^{-4} \text{ cm}^{-1}/\text{torr} \rightarrow 7 \times 10^{-3} \text{ cm}^{-1}$. If the lifetimes for the relevant transitions of CH_3F were one second, estimated for the forbidden transition,

and ~ 10 ms, estimated for the allowed transition, then the gain coefficients are

$$g_{\text{CH}_3\text{F}} \cong 0.004 \text{ cm}^{-1}$$

and

$$g_{\text{NH}_3} \cong 0.1 \text{ cm}^{-1}.$$

Both would be adequate for demonstrating stimulated emission at $16 \mu\text{m}$; the difference in the numerical results reflects the difference in the strengths of the allowed and forbidden transitions.

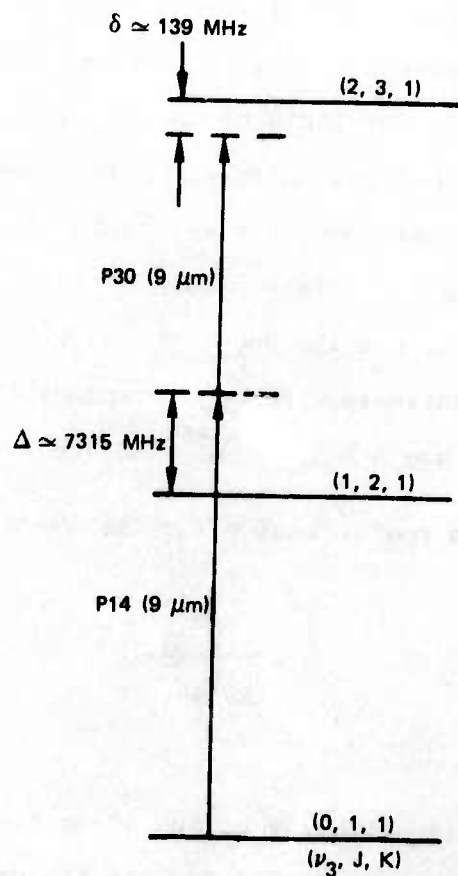


FIGURE 2 TWO-PHOTON TRANSITION IN THE ν_3 BAND OF $^{12}\text{CH}_3\text{F}$. The combination band (not shown) $2\nu_3 \rightarrow \nu_5$ falls in the $16\text{-}\mu\text{m}$ region.

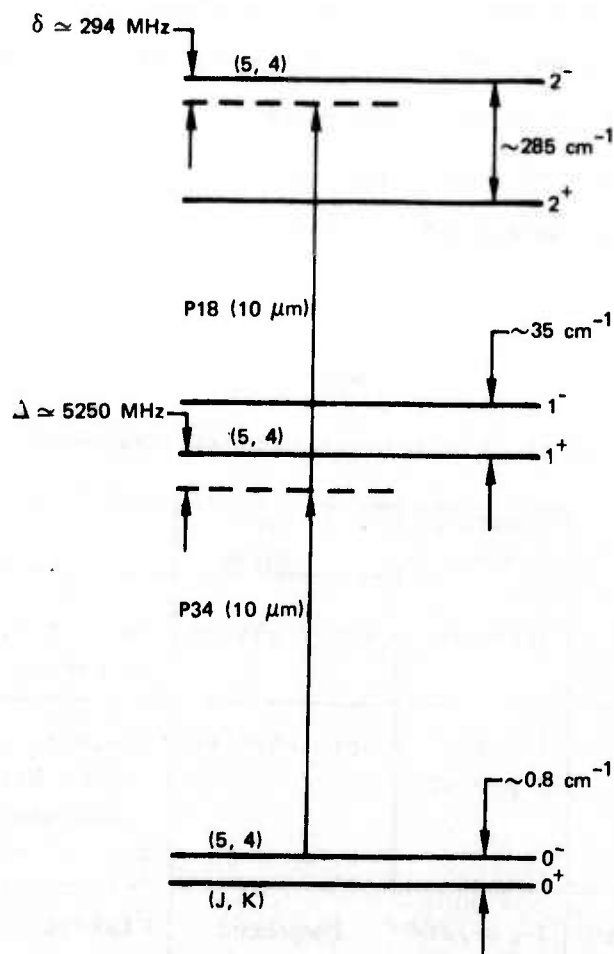


FIGURE 3 TWO-PHOTON TRANSITION IN THE ν_2 BAND OF $^{14}\text{NH}_3$.
The fully allowed $2^+ \rightarrow 1^-$ transitions fall in the 16- μm region.

2. Efficient Nonlinear Infrared Processes in Molecular Gases

Nonlinear optical processes in atomic vapors have been developed for shifting visible laser radiation toward the ultraviolet as well as to the near infrared. These processes include third-harmonic generation,^{54,55} four-wave mixing,⁵⁶ and stimulated Raman scattering.⁵⁶ They can be made more efficient by taking advantage of intermediate-state resonances to enhance the nonlinear susceptibility. Another nonlinear process, hyper-Raman scattering, has also been observed in spontaneous emission,⁴⁷ but

has not been made efficient by taking advantage of resonance. Generally, resonances involving one-photon transitions from the ground state are undesirable because of effects associated with single-photon absorption such as gas heating with concomitant destruction of phase matching. these processes are summarized in Table 5.

Table 5

SUMMARY OF NONLINEAR OPTICAL PROCESSES

Process	Possible Resonance	Phase Matching	Comments
Stimulated Raman	1-photon	Not required	Inelastic. Forward scatter to reduce Doppler broadening.
Hyper-Raman $\omega = \omega_L \pm \omega'_L - \omega_v$	1- and 2-photon	Not required	Inelastic. Can partially cancel Doppler. Two-photon resonance does not suffer from power broadening.
Third-order frequency conversion $\omega = \omega_L \pm \omega'_L (\pm) \omega''_L$	1-, 2-, and 3-photon	Required	Elastic. $\omega_L = \omega'_L = \omega''_L$ and + signs give third-harmonic generation. Two- and three-photon resonance does not suffer from power broadening.
Inelastic four-wave mixing $\omega_L - \omega = \omega_v = \omega'_L - \omega''_L$	1-photon	Required	ω''_L can be a third driving laser frequency or be stimulated Raman output. Excitation of medium can occur in visible, which then scatters infrared.

In this section we consider the applicability of these effects to the infrared, and also discuss other possibilities such as inelastic four-wave mixing. In the infrared the resonances generally involve the change of vibrational states and thus suffer from small-dipole matrix elements. Furthermore, for a given amount of nonlinear polarization, build-up lengths scale as the wavelength or wavelength squared. On the other hand, radiation sources in the infrared are available that are very efficient and have high powers. In Table 5 we list the processes considered, in the order of the number of photons involved. We restrict our attention to describing the processes and giving some numerical results. Where possible, the details are left to an appendix and to documents given in the List of References.

a. Stimulated Raman Scattering

Figure 4 shows the energy level and wave-vector conservation conditions associated with stimulated Raman scattering. Here, ω_L and ω are the input and output photon frequencies, respectively, ω_v and ω_v are the vibration-rotation frequencies, and ω_{ex} is an excitation frequency of arbitrary character; also, $\vec{k}_L$ and $\vec{k}$ are the input and output photon wave vectors, while $\vec{q}$ denotes the wave vector of the material excitation. The maximum gain is in the forward direction because of the reduction in Doppler width in forward scattering. In Appendix A, a calculation is given for resonant Raman scattering for a typical molecule, assuming a frequency mismatch of 1 cm^{-1} in the $10\text{-}\mu\text{m}$ region. The gain coefficient is found to be of the order of 10^{-3} cm/MW . This is of the same order as the off-resonant Raman gain in H_2 using a $1\text{-}\mu\text{m}$ pump. For a frequency mismatch of 0.1 cm^{-1} the gain coefficient becomes 10^{-1} cm/MW . To tune into resonance, Stark and Zeeman tuning of the molecules may be used as well as input-laser-line selection. Care must be taken to avoid the possibility of power broadening destroying the resonance.^{57,58}

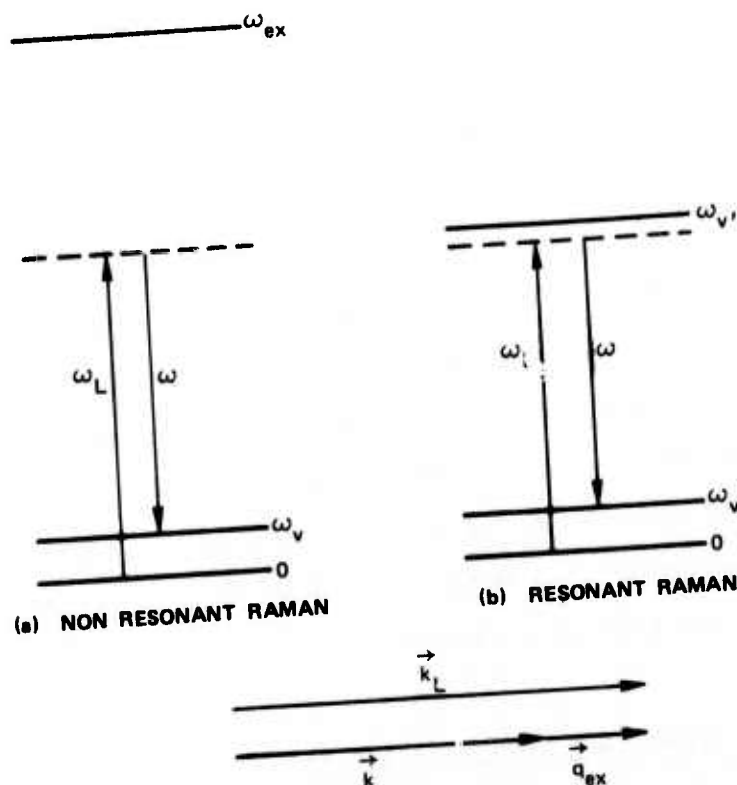


FIGURE 4 ENERGY-LEVEL DIAGRAMS AND WAVE-VECTOR CONSERVATION CONDITIONS FOR STIMULATED RAMAN SCATTERING

b. Hyper-Raman Scattering

Figure 5 shows the energy-level and wave-vector diagram for resonant hyper-Raman scattering. We have shown the case where two photons are absorbed and a single photon is emitted.⁵⁹ There is, of course, the analogous process in which a single photon is absorbed and two are emitted. For the process indicated there are smaller cross sections for cases in which there are fewer intermediate-state resonances than indicated in the diagram.

The hyper-Raman gain is related to the normal Raman gain by a factor of the form

$$\frac{g_{h-R}}{g_R} \approx \left(\frac{\mu' E'}{\hbar \delta \omega} \right)^2 \quad (27)$$

where μ' is the additional dipole matrix element and E' the additional electric field. We assume here that there is an additional near-resonance $\delta\omega'$ corresponding to the additional photon. The dipole matrix element can take on the value corresponding to a fully allowed transition. For $\mu' = 0.2$ Debye, $\delta\omega' = 1 \text{ cm}^{-1}$, and a laser intensity of 10^8 W/cm^2 , the ratio given above approaches unity. To make this process resonant for both input photons will likely require the input photons to be at different frequencies.

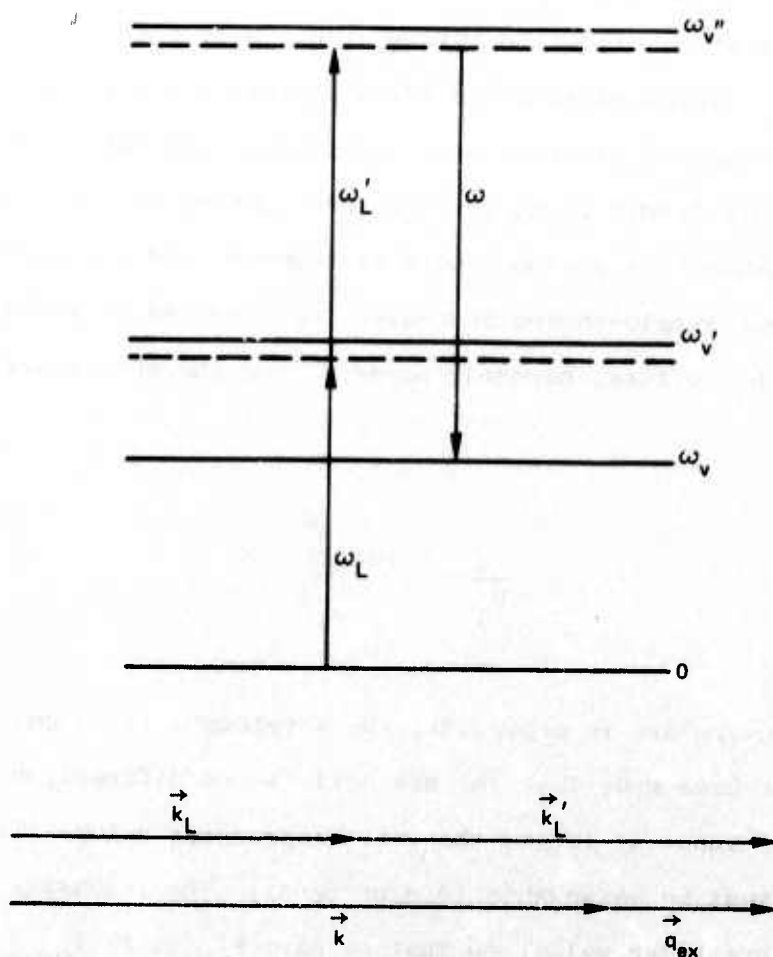


FIGURE 5 ENERGY LEVEL DIAGRAM AND WAVE-VECTOR CONSERVATION CONDITIONS FOR RESONANT HYPER-RAMAN SCATTERING

c. Elastic Third-Order Frequency Conversion

There are several sub-processes that can be considered.

1) Sum-Frequency Generation-Tripling

The simplest case is that of tripling as shown in Figure 6. This process is a particularly interesting one because it would allow the up-conversion of an efficient infrared laser (such as CO_2) to shorter wavelengths. For example, a 10.6- or 9.6- μm radiation can be directly converted to the 3.5-to-3.2- μm wavelength region. Up-conversion to 3.5 μm is significant because of the high atmospheric transmittance at sea level in this region. Ueda and Shimoda⁶⁰ have given a very straightforward and illuminating discussion of this process for single-frequency excitation of an harmonic diatomic. The result is valid when only linear terms in $\partial\mu/\partial x$ are considered. For $\partial\mu/\partial x$ at a value of 1 Debye/ $\text{\AA}$, a pressure of 1 atmosphere, and a mismatch of 1 cm^{-1} from the first single-photon resonance, we find the ratio of third harmonic power P_3 to first harmonic power P_1 for the phase-matched case to be

$$\frac{P_3}{P_1} \approx 10^{-14} \frac{P_1^2}{\lambda^4} \quad (28)$$

where the powers are in megawatts, the wavelength is in cm, and the assumption has been made that the gas cell is one diffraction length long. For 10 MW of input at 10 μm , the ratio approaches unity. The length of the cell l must be reasonable (3 m or less). The intensity should not exceed the breakdown value, so that we have $P_{\text{Max}} \approx l\lambda I_{\text{Breakdown}}$.

The nonlinear coefficient for the above result has been calculated for an anharmonic diatomic. There are a number of other interesting considerations. For example, there are molecular systems

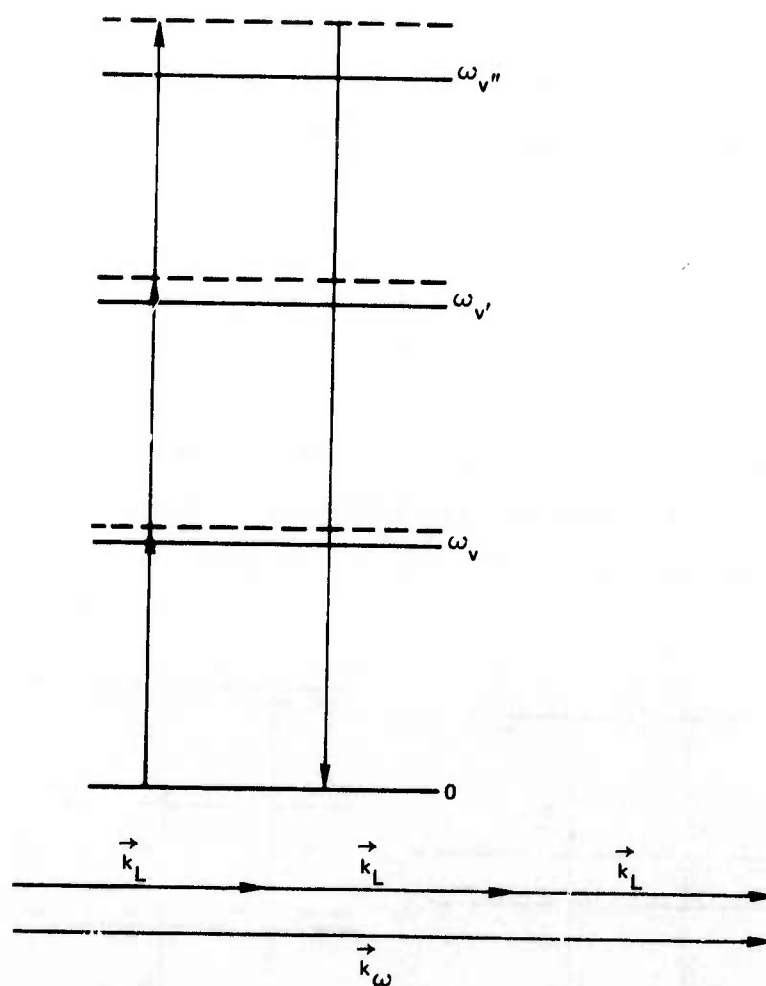


FIGURE 6 ENERGY LEVEL DIAGRAM AND WAVE-VECTOR CONSERVATION CONDITIONS FOR RESONANT TRIPLING

with large electrical anharmonicities, such as that which occurs in the ν_2 vibration of OCS, where terms such as $\partial^2 \mu / \partial x^2$ and $\partial^3 \mu / \partial x^3$ can make important contributions. Polyatomics increase the variety of vibrational excitations that may occur, including the possibility of a Fermi resonance between the third level of one normal mode and the first level of a second infrared active mode. Perturbations such as Fermi resonance and Coriolis coupling are important aspects of this problem. Unfortunately, little is known about higher levels in polyatomic molecules.

2) Elastic Four-Wave Mixing Processes

The same order of nonlinear susceptibility that gives rise to the sum-frequency generation process can also lead to processes in which new frequencies are generated as follows:

$$\omega = \omega_L + \omega'_L - \omega''_L \quad (29)$$

$$\omega = \omega_L - \omega'_L - \omega''_L \quad (30)$$

It is possible to make each step in the process resonant as shown in Figure 7. As can be seen, the process shown in Figure 7(b) is entirely analogous to sum-frequency generation or tripling.

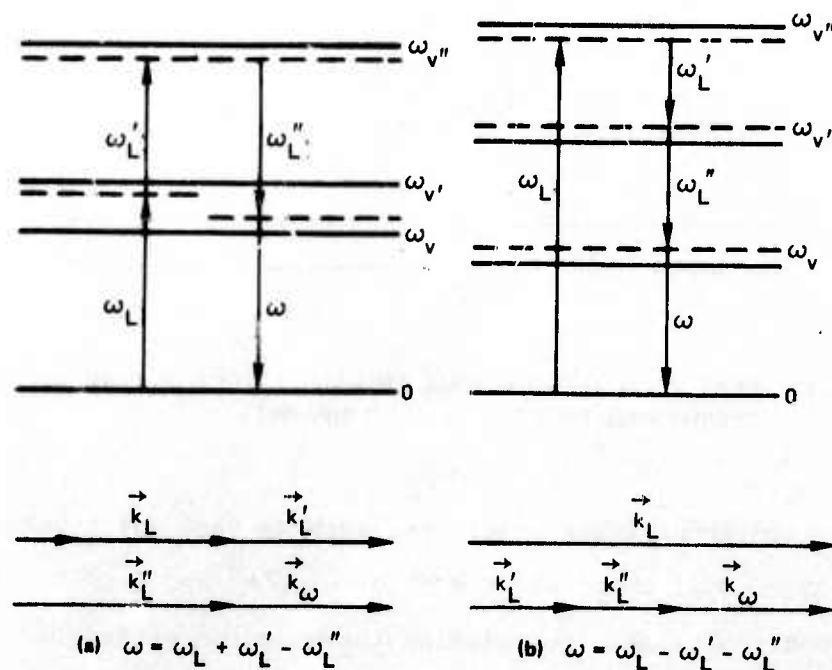


FIGURE 7 ENERGY-LEVEL DIAGRAMS AND WAVE-VECTOR CONSERVATION CONDITIONS FOR ELASTIC FOUR-WAVE MIXING PROCESSES

What is perhaps more interesting from the point of view of tunability is the possibility of level ω_v being far from resonance, and of tuning ω_L'' so that the output frequency is tunable. This effect has been observed for Process (30) shown in Figure 7(b). In this process, the energy levels were atomic and the fields corresponding to ω_L and ω_L'' were generated by dye lasers. The susceptibility is sufficiently large in this case that the field at ω_L' did not have to be introduced externally, but was generated by the stimulated Raman effect. For the molecular case, in Process (30) the presence of a Fermi resonance at levels ω_v'' or ω_v' would considerably enhance the effect. If resonant Raman scattering is obtained as described earlier in this section, then Process (30) should be readily observed. In Process (29) the steps indicated can be normal vibrational dipole transitions; the two upward steps are near-resonant, while the downward steps are nonresonant (to allow tunability of ω_L'' and ω). A rough estimate of the third-order nonlinear susceptibility for Process (29) is given by the following relation:

$$\chi^{(3)} \cong \frac{\alpha_L \lambda_L}{8\pi n} \frac{\gamma}{(\omega_L - \omega_v')} \left\{ \frac{\mu_{v'v''}}{(\omega_L' - \omega_v'' + \omega_v')} \right\} \left\{ \frac{\mu_{v''v}}{\omega_L'' - \omega_v'' + \omega_v'} \right\} \quad (31)$$

where α_L is the linear absorption coefficient on line center of the $o \rightarrow v$ transition, λ_L is the wavelength of this photon, γ is the linewidth of this transition, and the μ 's are the vibrational dipole matrix elements. When

$\alpha_L = 3 \text{ cm}^{-1}$, $\lambda_L = 10 \text{ }\mu\text{m}$, $\gamma = 0.1 \text{ cm}^{-1}$, $\omega_L - \omega_v' \approx 1 \text{ cm}^{-1}$, $\omega_L' - \omega_v'' + \omega_v' = 1 \text{ cm}^{-1}$, $\omega_L'' - \omega_v'' + \omega_v = 100 \text{ cm}^{-1}$, and $\mu_{v'v''} = \mu_{v''v} = 0.1 \text{ Debye}$, we find

$\chi^{(3)} \approx 10^{-14} \text{ esu}$. The output power of one diffraction length for an interaction distance is given by

$$P_\omega \approx 10^{-5} P_{\omega_L} P_{\omega_L'} P_{\omega_L''} \quad (32)$$

where the powers are in megawatts, and assuming that all the wavelengths are in the 10- μ m range. If the input powers are 10 MW, then 10 kW of power can be generated at frequency ω .

d. Inelastic Four-Wave Mixing

This process is closely related to the elastic processes considered in the previous section. The coherent vibrational/rotational excitation built up in one Raman process can be used to Stokes-Raman-shift⁶¹ radiation at another frequency ω_L as shown in Figure 8. The process can use only infrared-frequency photons [Figure 8(a)], or, by excitation in the visible, shifts can be produced in the infrared [Figure 8(b)]. This latter process is particularly interesting for the case of H_2 excitation by a visible or near-infrared laser, since thresholds of the order of 10 kW have been observed⁶² for stimulated scattering in the visible. In hydrogen the Raman linewidth is very narrow for both vibrational and rotational scattering, and the number of rotational states thermally occupied is small, resulting in a high gain coefficient.

The situation that is simplest to handle analytically is a parametric mixing process in which two short-wavelength laser beams (ω'_L, ω''_L) with a difference frequency equal to a H_2 Raman frequency are introduced into the H_2 along with the long-wavelength pump source (ω_L). In practice the two short-wavelength beams could be generated by stimulated Raman scattering in the H_2 from a single pump beam either in a single pass along with this mixing or in a resonator structure before the introduction of the long-wavelength pump laser beam. These systems have the advantage that no resonator optics at the output frequency ω are required. For a mixing process, phase-matching constraints must be satisfied. H_2 of course has very little dispersion in the infrared, and an additional negatively dispersive gas could always be added to satisfy this constraint; therefore, in what follows, phase-matching will be assumed.

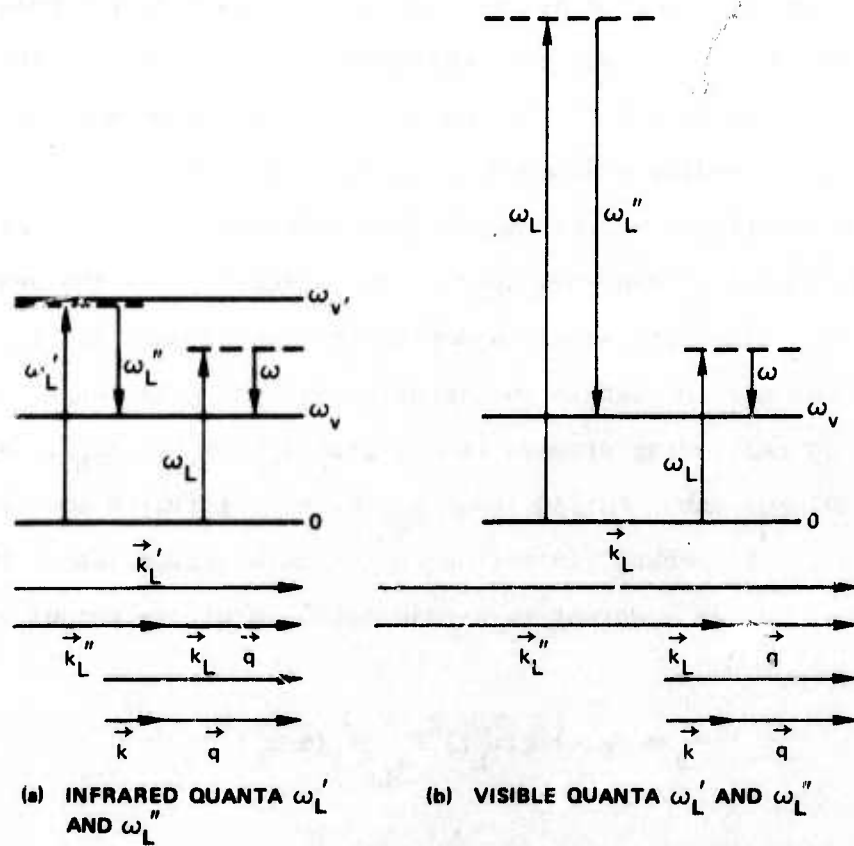


FIGURE 8 ENERGY-LEVEL DIAGRAMS AND WAVE-VECTOR CONSERVATION CONDITIONS FOR INELASTIC FOUR-WAVE MIXING PROCESSES

The intensity of the infrared Stokes wave is given by the expression

$$I_{\omega} = \frac{1}{4} g^2(\omega) I_{\omega_L} I_{\omega'_L} I_{\omega''_L} \ell^2 \quad (33)$$

where $g(\omega)$ (cm/MW) is the Raman gain coefficient at the infrared frequency ω , I_{ω_L} , $I_{\omega'_L}$, and $I_{\omega''_L}$ are the power densities of the infrared pump wave and the near infrared or visible pump and Stokes waves, and ℓ is the interaction length. This length is limited by the focusing properties of Gaussian beams just as in ordinary Raman scattering. An additional constraint on the interaction length arises because the four-wave mixing is effective only in the region of near 50% conversion efficiency for the near-infrared Raman process, since its strength depends on the product $I_{\omega'_L} I_{\omega''_L}$. This limits the interaction length to approximately the gain length for the near-infrared scattering process [$\ell \sim 1/g(\omega''_L) I_{\omega'_L}$, $I_{\omega'_L} \approx I_{\omega''_L}$]. With a 200-mJ flashlamp-pumped Nd:YAG laser as the near infrared source (~ 20 ns pulse width), this second limitation on the interaction length is the dominant one, and an order-of-magnitude estimate of the output power at ω is

$$P_{\omega} \cong [g(\omega)/g(\omega'_L)]^2 P_{\omega_L} = (\omega/\omega'_L)^2 P_{\omega_L} \quad (34)$$

independent of the near-infrared power levels. Then for the rotational Raman scattering case in H_2 , using a 200-mJ TEM₀₀ CO₂ pump laser, the output power is $P_{\omega} = 5$ kW for a pulse energy of 50 μ J. This energy conversion efficiency is low due to the poor temporal overlap between the two pump sources. Higher multimode powers are available and will result in additional power conversion, but at a reduced efficiency. Further, this conversion estimate is conservative since contributions from second- and higher-order Stokes processes have not been included; these will effectively extend the available gain length.

More elaborate schemes can also be considered in which the four-wave mixing is used only to bring the long-wavelength Stokes beam to an intensity well above noise level and so eliminate the buildup-time problems and allow the use of longer cavities and lower power densities.

3. Conclusions and Recommendations

The main conclusions and recommendations pertaining to this section are as follows:

- (1) It is anticipated that efficient conversion of currently available fixed-frequency sources (CO_2 , CO, HF/DF) can be achieved at high power levels.
- (2) Several processes are applicable for frequency conversion of infrared radiation in the wavelength region between 1 μm and 100 μm .
- (3) Multiphoton excitation is feasible, and non-linear processes facilitate the performance of up-conversion, a process generally not available through the technique of single-photon optical pumping.
- (4) Detailed spectroscopic data, especially pertaining to perturbed features of excited vibrational manifolds, are needed.
- (5) The use of gases permits the scaling to large volumes and energy throughputs, with material damage considerations minimized.
- (6) An effort of approximately 10 scientists (supported) distributed to cover items 1 through 5 above is recommended. The support in this area has capital intensive characteristics.

D. Far-Infrared and Submillimeter Radiation*

Progress has been made in the last few years⁶³ in developing new

* This section was prepared by H. Fetterman.

laser systems in the far-infrared and submillimeter regions that operate by optical pumping. In this region, where photon energies are less than kT , it has been extremely difficult to achieve population inversion by conventional techniques such as electrical discharges.⁶⁴ Optically pumped molecular lasers successfully eliminated this problem by using highly monochromatic pump radiation in close coincidence with particular absorption lines of the amplifying media. As a consequence of this new technique it has become possible to extrapolate from the early results and to predict high-power pulsed⁶⁵ and CW lasers at almost any far-infrared wavelength.

The initial projections of high powers⁶⁶ and multiplicity of wavelengths have been realized to some extent. Current research, however, is predominantly oriented⁶⁷ toward an experimental search effort, with laser action usually obtained in complex molecules having virtually unknown level structures. This type of effort is inherently self-limiting and does not generate optimal systems. To date, the best quantum efficiencies in these lasers are over two orders of magnitude down from Manley-Rowe limits.

1. State of Present Technology

As an example of a typical far-infrared optically pumped laser we consider methyl fluoride (CH_3F). The energy-level diagram⁶³ in Figure 9 indicates the origin of laser emission from a typical symmetric top molecule. Nearly coincident with the transitions (ν_3 , J, K) = (0,12,1) $\rightarrow$ (1,12,1) and (0,12,2) $\rightarrow$ (1,12,2) of the ν_3 vibrational mode of CH_3F , the P(20) CO_2 line of the 9.6- μm branch selectively depletes the J = 12 levels in the ground state and creates rotational excited levels in the first vibrational state. This molecule has a permanent dipole moment, and far-infrared oscillation is obtainable between the inverted levels J = 12 $\rightarrow$ J = 11 in $\nu_3 = 1$ and J = 13 $\rightarrow$ J = 12 in $\nu_3 = 0$. In many systems, laser action on the cascades (1, J-1, K) $\rightarrow$ (1, J-2, K) has been achieved.⁶⁸

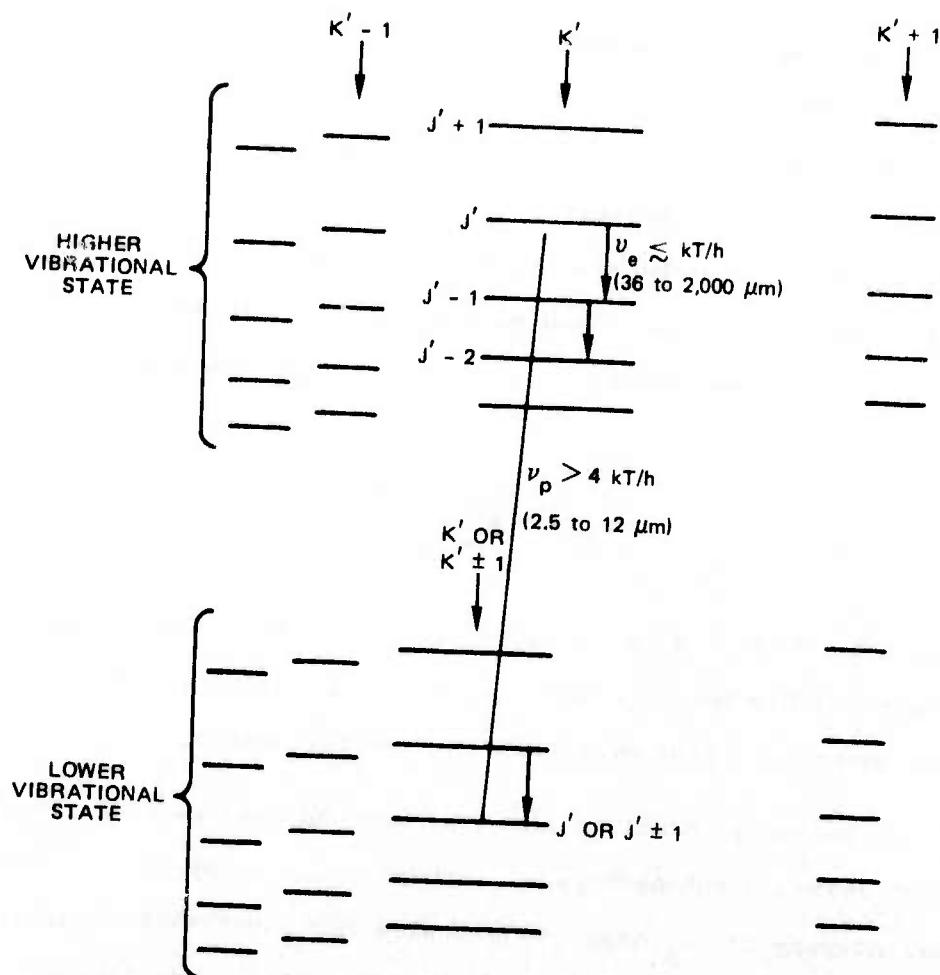


FIGURE 9 PARTIAL ENERGY-LEVEL DIAGRAM FOR A TYPICAL SYMMETRIC TOP MOLECULE ILLUSTRATING TRANSITIONS IN AN OPTICALLY PUMPED SUBMILLIMETER-WAVE LASER

Analysis of the rate equations appropriate for those optically pumped lasers shows that in addition to the stimulated emission, V-V collisions coupling the ν_3 and ν_6 modes and V-T relaxation processes (as well as rotational-rotational and rotational-translational interactions) play important roles in the distribution of energy throughout the entire vibrational manifold.⁶⁹ These transfer processes effectively determine the output powers and efficiency of the far-infrared lasers, and merit intensive study. It is probable, for example, that the addition of buffer gases can be used to help optimize the systems by selectively increasing certain relaxation rates.

An excellent example of this type of optimization is demonstrated in the development of a waveguide laser.⁷⁰ This type of laser uses oversized metallic waveguides for a cavity and offers lower losses and easier construction than conventional resonators. However, its real significance becomes apparent from the rate equations. The solutions of these equations show that spatial diffusion and wall collisions are important relaxation mechanisms for CW operations. In fact, the power output in the far infrared should go as⁷¹

$$P_{\text{FIR}} \propto P_{\text{pump}}^n D^{-2n} L^2 \quad (35)$$

where $n = 1.1 \sim 1.5$, D is the diameter, and L is length of the resonator. This relationship has been verified by Tanaka et al.,⁷¹ who have obtained 20-fold power increases over conventional resonators.

The very selective excitation of optical pumping creates requirements of suitable coincidences. Several recent experiments⁶⁵ with the optical pumping of NH_3 have demonstrated the importance of detailed molecular studies in satisfying these constraints. Because of the excellent spectral measurements of the transitions of the NH_3 molecule relative to the frequencies of the CO_2 laser, it has been possible to establish the techniques of off-resonant pumping and Stark tuning. By saturation of a molecular absorption far from the line center (off-resonant pumping), the constraints of coincidence between molecular absorber and laser pump are substantially reduced in the limit of high powers. In the regime of low-power CW pump sources, coincidence has been achieved by Stark-tuning the molecular levels to the pump frequencies. Both of these experiments indicate that with appropriate spectroscopic structure and rate studies, very advanced laser systems are possible. Further evidence of the efficiency of this approach is found in new experiments in D_2O ⁷² and 1,1 difluoroethylene.⁷³

Super-radiant far-infrared lasers⁷⁴ have been constructed that produce powers ranging up to 0.5 MW. The mechanism for generating this intense radiation is not well understood, since several gases that oscillate extremely well in conventional cavities, such as methanol, formic acid, and dimethyl ether, exhibit no super-radiant conversion. Others, such as CH_3F , NH_3 , and D_2O , that do generate the super-radiant mirrorless outputs have an unexplained temporal behavior, with delays of up to 3 μs from the pump pulse. Studies of these systems in terms of Dicke⁷⁵ super-radiance would be interesting both from the point of view of molecular kinetics and increased power levels.

A number of innovations have been made in the engineering of these lasers to improve performance and provide some degree of tunability. One of these is a pumping scheme that transversely couples the high-power pump beam by using cylindrical mirrors while still maintaining an efficient far-infrared cavity. Oscillation in this system⁷⁶ can be obtained far from the center of the homogeneously broadened line with a bandwidth demonstrated to be greater than 455 MHz.

Concurrent with the advent of optically pumped lasers has been the development of room-temperature Schottky⁷⁷ diode detectors having NEPs better than 10^{-16} watts Hz. By the use of such heterodyne detectors, new applications for far-infrared lasers have been found in radio astronomy, plasma diagnostics, and solid-state spectroscopy. In all of these areas, measurements made at far-infrared wavelengths cannot be obtained by any other means. The very first efforts in these fields have already revealed new, unanticipated phenomena.⁷⁸

Many of the techniques and studies required for optically pumped far-infrared laser development are also valuable in the near and middle infrared. Indeed, a brief glance at the major far-infrared researchers shows that virtually all have also contributed to optically pumped systems

at shorter wavelengths.^{79,80} This undoubtedly reflects the fundamental molecular studies and instrumentation common to both spectral regions.

Literally hundreds of new laser lines have now been generated between 30 and 2,000 μm using optical pumping to invert rotational population levels. The average spacing between the available far-infrared laser lines is already on the order of a fraction of a wavenumber, with peak powers ranging up to megawatt levels. Our examination reveals that only these optically pumped molecular lasers have the potential of high power, stability, and narrow linewidth required by most projected applications. Increased emphasis along the lines suggested below should produce major advances and useful systems. In addition, compact systems, tunable lasers, integrated optical devices, and even distributed-feedback lasers are all viable possibilities at these wavelengths.

A number of applications for military needs have been suggested ranging from secure communications to high-resolution radars. Most of these suffer from atmospheric attenuation and are clearly marginal with presently available devices. Additional development and propagation studies are required before any military application such as high-resolution radars or secure communications can be projected. However, significant improvements in the laser technology and their detectors are capable of dramatically changing this. Immediate applications of this technology are primarily in basic research and in plasma studies. Therefore, we see a well-defined purpose for increasing exploratory research in this field.

2. Future Directions

For continued progress in the field, efforts are indicated in the following areas:

- (1) Identification and optimization of systems for high-power operation. This should be a systematic effort

including a study of the kinetics and spectroscopy of the oscillating medium. Other related processes⁸¹ such as stimulated resonant Raman scattering from rotational levels should also be investigated.

- (2) Cavity design stressing use of gratings, appropriate dielectrics, and semitransparent meshes. Systems that incorporate the optically pumped cell directly into the pump's laser cavity have potentially high efficiency. The mating of a wide-bandwidth capillary CO₂ laser (CW or TEA) to a waveguide infrared laser is a logical need for the designing of compact, usable lasers.
- (3) Development of tunable optically pumped molecular lasers at useful wavelengths. Because of the high atmospheric absorption it is desirable to have a tunable far-infrared source able to oscillate at optimal frequencies for transmission. Most of the suggested techniques for tunable far-infrared lasers depend on either the pumping of these molecular gases at sufficiently high pressures, or the Stark tuning of rotational levels relative to each other. The feasibility of both of these techniques has recently been verified. A coordinated study of atmospheric propagation of these tunable lasers would greatly enhance this effort.

3. Conclusions and Recommendations

The main conclusions and recommendations of this section are:

- (1) Optically excited far-infrared molecular lasers are capable of generating peak power levels of megawatts with average powers of several watts. No other technique presently available can achieve these levels.
- (2) Potential developments include compact systems (waveguide structures, etc.), improved detectors, and far-infrared integrated optical structures.
- (3) There is a need for high-resolution spectroscopy and energy-transfer data for optimizing and developing advanced systems.

- (4) On account of the absence of clear major applications, an expended effort in this area is not indicated. The resources should remain at essentially the current level.

E. Electronic-Vibrational Energy Transfer Process*

1. General

Electronic energy can be utilized to populate levels that radiate in the infrared. Closely spaced atomic levels, such as those arising from fine-structure splittings or highly excited atomic states, can be used directly if an appropriate mechanism for excitation can be found. Systems of this nature are discussed in Appendix B. An alternative use of electronic energy in the production of infrared radiation involves the coupling of electronic and vibrational motions. This approach is discussed below.

The possibility of producing inverted populations on vibrational levels by using electronic-to-vibrational energy-transfer collisions is suggested by some recent observations showing that the fraction of available energy that is deposited in vibrational states can be substantial. It has been known for a long time that electronically excited states of atoms are rapidly quenched by molecules, and in several cases rate coefficients have been measured.⁸² However, the disposition of the energy transferred among the vibrational, rotational, and translational degrees of freedom is not generally known and only recently has the vibrational population distribution been examined for a few cases.

2. Current Status

The cross sections for quenching of the resonance states of a number of metal atoms such as the alkalis and Hg have been measured in

* This section was prepared by D. C. Lorents and R. Novick.

several laboratories.⁸³⁻⁹¹ There is considerable quantitative disagreement, but recent measurements for $\text{Hg}(^3\text{P}_1)$ and $\text{Hg}(^3\text{P}_0)$ quenching cross sections are converging to common values. These cross sections are listed in Table 6. We note that the total cross sections for quenching by molecules range between 1 and $60 \text{ \AA}^2$.

Table 6

MOLECULAR QUENCHING CROSS SECTIONS* OF Hg AT 300°K

Molecule	$^3\text{P}_1$ (Total)	$^3\text{P}_1 \rightarrow ^1\text{S}$	$^3\text{P}_1 \rightarrow ^3\text{P}_0$	$^3\text{P}_0 \rightarrow ^1\text{S}$	References
H_2	24.6	--	--	--	85
N_2	0.73	$\leq 4 \times 10^{-3}$	--	$\leq 2 \times 10^{-6}$	85,88,90
NO	25	20	5	8	87
O_2	60.5	--	--	--	85
CO	21.7	21	2.1	0.7	85,87,88,91
CO_2	10.2	--	--	--	85

* Cross sections given in units of 10^{-16} cm^2 .

Of the molecules that have been studied, it is only for the example of CO that some understanding of the distribution of the transferred energy has been obtained. Since the $\text{Hg}(^3\text{P}_1)$ is mainly quenched to the ground state in collision with CO (see Table 6), about 4.9 eV is available to be distributed among vibrational, rotational, and translational degrees of freedom. Unfortunately, the resulting initial CO vibrational population has been measured only for $^3\text{P}_0$ transfer,⁹² and not for the $^3\text{P}_1$ state which has the large cross section. The distribution is peaked at $v = 5$ and ranges from $v = 2$ to $v = 8$. Thus, on the average only 27% of the available $^3\text{P}_0$ energy is converted to vibrational

excitation. It would be very informative to have a good measurement of the $\text{CO}(\nu)$ distribution resulting from $\text{Hg}(^3\text{P}_1)$ deactivation. Earlier measurements⁹³⁻⁹⁵ of the vibrational distributions resulting from $\text{Hg}^*(^3\text{P}_1, ^3\text{P}_0)$ transfer to CO, NO, and HF apparently were influenced by the effect of V-V transfer at the densities used.

There have also been several studies of E-V transfer from $\text{Na}(^2\text{P})$ to N_2 and CO.^{84, 96-99} For $\text{Na}(^3\text{P}) + \text{N}_2$ there is now reasonable agreement among the available experiments that the energy is transferred mainly to $\nu = 4, 5$, and 6, indicating that about 70% of the electronic energy is converted to vibrational energy. In this case the cross section is $41 \text{ \AA}^2$ at room temperature,⁹⁷ so that rapid transfer is possible. Since $\text{Na}(^3\text{P})$ can be easily excited by electrons in a discharge, this offers a possible alternative to direct electron pumping of vibrational levels that may be advantageous, particularly in cases other than N_2 or CO where the molecular vibrations may be only weakly excited by electron collisions.

In other systems, the measured fractions of the energy delivered to vibration in an E-V transfer collision are listed in Table 7. In these cases, only the total energy transferred to vibration has been measured, and the initial distribution of vibrational quanta is unknown.

The last three entries in Table 7 involving reactions of $\text{CO}(a^3\pi)$ and $\text{CO}(d^3\Delta)$ are the first measurements on transfer from molecular electronic levels and show remarkably high conversion efficiencies. These examples demonstrate that very high E-V conversion efficiencies can be realized. There are undoubtedly many other currently unknown efficient E-V transfer reactions, some of which will be either directly or indirectly involved in various laser media.

Serious theoretical work on the problem of E-V energy transfer is just beginning. Early theoretical efforts^{102,103} attempted to describe the process in terms of an impulsive collision, but the prediction of this

model are contrary to experimental observations. Recently, the importance of molecular complex formation in collisions of this type has been recognized,¹⁰⁴ and detailed calculations on the system $O(^1D) + N_2 \rightarrow O(^3P) + N_2^{\ddagger}$ appear to be in much better accord with experiment. Fortunately, the semiclassical treatment of surface-crossing problems is progressing rapidly and now provides considerable simplification in the computational aspects of such problems.¹⁰⁵

Table 7

E-V ENERGY TRANSFER EFFICIENCY AND RATE-CONSTANT DATA

Reaction	Efficiency (%)	Total Quenching-Rate Constant (cm ³ /s)	Reference
$O(^1D) + N_2$	33	5×10^{-11}	99
$O(^1D) + CO$	40	3×10^{-11}	99
$CO(a^3\pi) + CO$	89	10×10^{-11}	100
$CO(d^3\Delta) + CO$	62	12×10^{-11}	100
$CO(d^3\Delta) + N_2$	96	3.6×10^{-11}	100

To be useful as a laser pump, not only must the E-V process be efficient, but we must have an efficient scheme of producing the electronic excitation. Low-pressure Na and Hg resonance lamps are well known to be very efficient, although high-power applications of such sources do not appear feasible. Species such as $CO(a^3\pi)$ and $N_2(A^3\Sigma)$ can be produced by energy-transfer processes in e-beam pumped rare gases with efficiencies up to 25%, which, when combined with the 85% quantum efficiency in the case of CO, would yield 20% overall efficiency. Thus,

this technique seems to be a viable alternative method of pumping vibrational levels that merits further examination. The alkali ^2P levels can be efficiently pumped in a discharge, and since the effective transfer from these levels to N_2 and CO is demonstrated, this technique may be promising.

Although we have discussed the E-V process in terms of CO and N_2 , for which we have most information, it is undoubtedly applicable to many diatomic or triatomic molecules. In fact, it may be possible to use this pumping technique for molecular systems such as CN, NO, HCN, CS_2 , and others. Apparently there has not been any study of E-V transfer to triatomics.

It should also be noted that the E-V process discussed here is essentially the reverse of the V-E conversion discussed in the 1974 Summer Study¹ (Section III-A-5). The physical mechanisms of these two processes are closely related so that study of one of these processes provides some information about the other, and therefore any studies of these issues should be coordinated. In addition, it should be noted that E-V and V-E processes play an important role in many chemical and discharge laser systems.

3. Conclusions and Recommendations

The basic findings of this section are the following:

- (1) The initial vibrational-state distributions arising from E-V reactions and the efficiency of such transfer should be measured for several promising systems. These are critical data needed to evaluate laser possibilities.
- (2) A theoretical model for E-V transfer has been developed recently and applied successfully to the case of $O(^1D) + N_2$ transfer. These calculations require knowledge of the excited states and couplings characteristic of excited triatomic

surfaces. Since triatomic surfaces were a topic recommended in the 1974 Summer Study, this area should be included under that recommendation.

- (3) In summary, we believe that there is a reasonable probability that E-V transfer processes may play a central role in the development of certain new IR lasers. We recommend that a modest effort to implement Suggestions 1 and 2 above be undertaken. A small effort at a maximum of two scientists appears adequate, and should be added to the recommendations contained in Sections IV-B and IV-G of the 1974 Summer Study.¹

F. Electron Excitation of Molecules*

1. General

Collisions of electrons with molecules can lead to a variety of product configurations including rotational, vibrational, or electronic excitation, dissociation, attachment, and ionization. In most cases more than one degree of freedom is simultaneously excited. In relation to laser media, electron scattering processes play at least two very important roles. Firstly, electron production and loss mechanisms (e.g., ionization, recombination, and attachment) establish the electron density n_e and velocity distribution $f(v)$ for specified conditions of excitation. It follows, conversely, that a knowledge of the collisional cross sections will enable the control and engineering of the desired distribution function. Secondly, the electrons can couple directly to produce the population inversion of the gain medium. The best known examples are the CO_2 and CO EDL systems. The power, P , coupled into the upper state of the laser medium is given by the expression

$$P = \alpha \int n_e f(v) Q(v) d^3 v \quad (36)$$

* This section was prepared by C. K. Rhodes.

where $Q(v)$ is the cross section of the relevant inelastic amplitude. Therefore, if we wish to evaluate or optimize the quantity expressed in Eq. (36), we require quantitative knowledge of the processes determining both n_e and $f(v)$ as well as the specific cross section $Q(v)$, which couples to the upper laser level.

2. Current Status

Extensive data concerning the excitation of atoms¹⁰⁶ and diatomics^{107,108} are available and are the subjects of extensive reviews. Considerable data also exist for recombination.¹⁰⁹ Furthermore, these data have been successfully integrated with the Boltzmann equation in the description of laser devices in both the infrared¹¹⁰ and ultraviolet¹¹¹ spectral regions. These treatments are definitely adequate for the intended purpose and demonstrate that the body of existing data on these relatively simple systems is not seriously deficient. This, of course, does not rule out specific cases where a need may arise. Polar systems, such as HCl, may be such an example.

Data on triatomics and larger systems form an image sharply contrasting with the picture describing the situation for atoms and diatomics presented above. In this case there are more molecules and fewer measurements, a condition paralleling the findings on electronic structure that were noted in the 1974 Study.¹ For instance, although measurements on CO₂ for momentum transfer,^{112,113} vibrational excitation,¹¹⁴ ionization,¹¹⁵ and attachment¹¹⁶ are available, the corresponding data are largely absent, except in a relatively few isolated cases, for other polyatomic systems.

Molecular stability of polyatomic species under discharge conditions is an important consideration. An example is given by the comparison of CO₂ and N₂O in which the latter has a far greater dissociative

attachment rate^{113,116,117} under the plasma conditions of interest. These rates may be the determining parameters in establishing gas-flow conditions and could be a major factor in the chemistry of any system utilizing an isotopic molecule of normally low abundance.

General processes involving electrons that affect the molecular lifetime are dissociative attachment



and direct collisional dissociation



The amplitudes for these reactions are sensitive to the electron energy, and often depend strongly on level of vibrational excitation of the system AB. Measurements of vibrational ground-state values may not apply under the plasma conditions of practical interest. The ability to control the electron distribution function $f(v)$ by collisional means can, therefore, exert considerable influence on the importance of these processes.

3. Conclusions and Recommendations

- (1) Canonical electron-scattering measurements emphasizing vibrationally inelastic channels should be extended to polyatomics (stressing triatomics) and polar diatomics.
- (2) An examination of polyatomic dissociative modes should be made because they affect molecular stability and practical usefulness (e.g., isotopic laser systems).
- (3) Although these data are important in laser design, the current data base does not seem critically lacking. It is recommended that the activity in this area be supported to maintain the present national level. No expansion of effort is indicated.

Appendix A

VIBRATIONAL RESONANCE RAMAN SCATTERING

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Appendix A

VIBRATIONAL RESONANCE RAMAN SCATTERING*

Optical pumping of molecules can be an efficient technique for generating new infrared laser frequencies. Laser action on vibrational transitions has been demonstrated in several diatomic and triatomic molecules either by direct optical excitation or by resonant transfer of vibrational energy from another molecular species that has a better frequency match with the pump laser. For polyatomic molecules it is generally more difficult to obtain population inversion because of the rapid cross-relaxation between the vibrational modes. Furthermore, the laser threshold is often increased due to a thermal population of the lower laser level. We will therefore consider resonance Raman scattering as an alternative method for infrared frequency generation. The efficiency of this process is independent of the relaxation time of the intermediate state, and excited-state absorption is negligible since the Raman output frequency does not coincide with the absorption frequency.

We consider the three-level system shown in Figure 4(b). Here o , v , and v' represent different vibrational levels and ω_L and ω are, respectively, the pump and Stokes Raman frequency. The general expression for the transition probability for Raman scattering is given by

$$W_{fi} = \frac{2\pi}{\hbar} \left| \sum_m \frac{(f|H'|m)(m|H'|i)}{(E_i - E_m)} \right|^2 \delta(E_f - E_i) \quad (A-1)$$

* This appendix was prepared by H. Kildal.

where i and f refer, respectively, to the initial and final state. Using this expression we can calculate the Raman gain coefficient, which, in mks units, is given by

$$g_{\text{ram}} = (2\pi)^3 \left(\frac{1}{4\pi\epsilon_0 \hbar c} \right) \omega I_L \left| \sum_{v'} \frac{(v|\mu|v')(v'|\mu_L|o)}{\omega_L + \omega_{ov'}} - \frac{(v|\mu_L|v')(v'|\mu|o)}{\omega + \omega_{v'o}} \right|^2 (N_o - N_v) \rho_F \quad (\text{A-2})$$

where I_L is the pump intensity, μ_L and μ are the projections of the dipole operator in the direction of the pump and Stokes field, respectively, and N_x is the number of molecules per unit volume in the x state. Also, $\rho_F = 2/(\pi\hbar\Delta\omega)$ where $\Delta\omega$ is the linewidth. When ω_L is in close resonance with the $o \rightarrow v'$ transition, the second nonresonant term in the gain expression can be neglected and we obtain:

$$g_{\text{ram}} = (2\pi)^3 \left(\frac{1}{4\pi\epsilon_0 \hbar c} \right)^2 \frac{\omega}{(\delta\omega)^2} \left| \langle \mu \rangle_{vv'} \langle \mu_L \rangle_{v'o} \right|^2 I_L (N_o - N_v) \frac{2}{\pi\hbar\Delta\omega} \quad (\text{A-3})$$

where $\delta\omega = \omega_L + \omega_{ov'}$. The Raman gain expression can also be rewritten as

$$g_{\text{ram}} = a_{\text{off}}^{ov'} a_{\text{on}}^{vv'} \frac{I_L}{\hbar\omega_L \Delta\omega N_v} \quad (\text{A-4})$$

where

$$a_{\text{off}}^{ov'} = (2\pi) \left(\frac{1}{4\pi\epsilon_0 \hbar c} \right) \frac{\omega_L \Delta\omega}{(\delta\omega)^2} \left| \langle \mu_L \rangle_{v'o} \right|^2 N_o \quad (\text{A-5})$$

is the off-center absorption coefficient for the $0 \rightarrow v'$ transition and

$$a_{\text{on}}^{vv'} = (8\pi) \left(\frac{1}{4\pi\epsilon_0 \hbar c} \right) \frac{\omega}{\Delta\omega} \left| \langle \mu \rangle_{vv'} \right|^2 N_v \quad (\text{A-6})$$

is the on-center absorption coefficient for the $v \rightarrow v'$ transition. In Eq. (A-4) it has been assumed for simplicity that $N_o \gg N_v$.

For a numerical example we choose the following values:

$$\langle \mu_L \rangle_{ov'}^2 = 0.03 D^2$$

$$\langle \mu \rangle_{vv'}^2 = 0.0006 D^2$$

$$\nu_L/c = 1000 \text{ cm}^{-1}$$

$$\nu'/c = 630 \text{ cm}^{-1}$$

$$\delta\nu = 30 \text{ GHz}$$

$$\Delta\nu/p = 10 \text{ MHz/torr}$$

$$N/p = 3.54 \times 10^{22} f(m^{-3} \text{ torr}^{-1})$$

where f is a Boltzmann factor. By insertion into Eqs. (A-4), (A-5), and (A-6) we obtain

$$g_{\text{ram}} = 5 \times 10^{-8} I_L f_o (W^{-1} \text{ cm}) \quad (\text{A-7})$$

$$a_{\text{off}}^{ov'} = 7 \times 10^{-5} p^2 f_o (\text{torr}^{-2} \text{ cm}^{-1}) \quad (\text{A-8})$$

$$a_{\text{on}}^{vv'} = 32 f_v (\text{cm}^{-1}) \quad (\text{A-9})$$

When the linewidth is determined by pressure-broadening, the Raman gain is pressure-independent. However, in order to reduce the direct absorption into the v' state, the pressure should not be higher than to make the pressure width comparable to the Doppler width, which corresponds to a pressure of approximately 10 torr. Assuming the Boltzmann factor $f_o = 0.02$ and $I_L = 10^8 \text{ W/cm}^2$, the calculated gain is

$$g_{\text{ram}} = 0.1 \text{ cm}^{-1}$$

which should be sufficient for laser Raman action in a cavity. The Raman gain must overcome the absorption between the v and v' states. At the Raman frequency the absorption constant is

$$a_{\text{off}}^{vv'} = a_{\text{on}}^{vv'} \frac{(\Delta\omega/2)^2}{\delta\omega}$$

or

$$a_{\text{off}}^{vv'} = 9 \times 10^{-7} f_v \text{ cm}^{-1}$$

for $\delta v = 30 \text{ GHz}$, so that the excited-state absorption is negligible.

It is interesting to compare the Raman process with the direct off-resonance optical pumping technique. Neglecting saturation and assuming a pulse length much longer than the nonradiative deactivation time $\tau_{v'}$ of the v' state, we find that the number of excited molecules is given by

$$N_{v'} = a_{\text{off}}^{ov'} \frac{I_L \tau_{v'}}{\hbar\omega_L} \quad (\text{A-10})$$

Substituting this into the expression for the gain g at the line center of the $v \rightarrow v'$ transition we obtain

$$\begin{aligned} g &= a_{\text{on}}^{vv'} \left(N_{v'} / N_v - 1 \right) \\ &= g_{\text{ram}} \Delta\omega\tau_{v'} - a_{\text{on}}^{vv'} \quad (\text{A-11}) \end{aligned}$$

In the case of rapid relaxation of the v' state ($\Delta\omega\tau_{v'} \sim 2$), the gain for off-resonance optical pumping is approximately equal to the Raman gain except that the absorption losses are higher because the oscillation occurs at the line center. Therefore, with any significant population in the lower laser level the Raman process will have the highest gain.

Power broadening of the $o \rightarrow v'$ transition has been neglected in the above example. It can be included in the expressions for the Raman gain and absorption in Eqs. (A-3) and (A-5) by replacing the $(\delta\omega)^2$ with $(\delta\omega)^2 + (\Delta\omega_p/2)^2$ where $\Delta\omega_p$ is the linewidth due to power broadening given by

$$\Delta\omega_p = \frac{2}{\hbar} \sqrt{\frac{I_L \Delta\omega_{v'}}{\epsilon_0 c}} \langle \mu_L \rangle_{ov'} \quad (A-12)$$

With numerical values from the previous example, $\Delta v_p = \Delta\omega_p/2\pi = 48$ GHz. Since $\Delta\omega_p/2$ is slightly smaller than $\delta\omega$, power broadening is not significant to our results. However, power broadening would limit the gain if the pump laser was brought closer into resonance with the $o \rightarrow v'$ transition.

In the above example the magnitude of the matrix element for the $o \rightarrow v'$ transition is typical for a direct vibrational transition, while the smaller $v \rightarrow v'$ matrix element corresponds to a cross-over transition between two different vibrational modes. It is possible, however, to consider a system where the $o \rightarrow v'$ transition has the smallest matrix element. For example, $o \rightarrow v'$ may be the first overtone of the $o \rightarrow v'$ vibrational transition. In this case the pump laser can be brought closer to resonance such that a ten-to-one-hundred-fold increase in the Raman gain coefficient should be possible.

Appendix B

ELECTRONIC-STATE INFRARED LASERS

Appendix B

ELECTRONIC-STATE INFRARED LASERS*

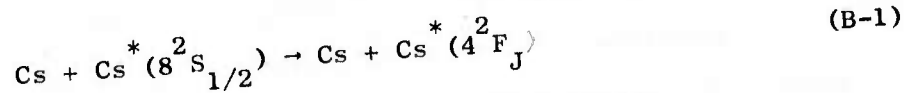
While it is customary to consider low-lying vibrational and rotational states for infrared laser action, it is important to recognize that there are a number of important examples of infrared lasers that operate between close-lying, highly excited electronic states. Although the quantum efficiency of such devices may be high, the energy efficiency is necessarily low. A possible solution to this problem would exist if one could find a vibrational system that is efficiently pumped to a high energy level by an electronically excited system. This aspect is considered in Section III-E. Vibrational-vibrational transfer collisions would rapidly transfer the excess population to a low vibrational state with negligible loss of energy, and hopefully laser action would occur via a low-lying transition.

An important possibility for these excited-state lasers that does not seem to have been exploited is Stark tuning. Since the state separations are small and the state density high, the Stark effect will be particularly large even in atoms, and significant tuning can be obtained with fields of the order of only a few tens of kilovolts per centimeter.¹¹⁸ In this section we will briefly review a number of existing infrared laser systems that utilize highly excited systems.

Historically, one of the first proposals for laser action involved electronic transitions between close-lying alkali states with high electronic excitation. As an example of this, we note the helium-pumped

* This appendix was prepared by R. Novick.

cesium system in which the cesium from the ground $6^2S_{1/2}$ to the $8^2P_{1/2}$ state by the helium 3888-Å line. In this system inversion occurs between the $8^2P_{1/2} \rightarrow 8^2S_{1/2}$ states and the $8^2P_{1/2} \rightarrow 6^2D_{1/2}$ states. The wavelength of the former is 3.21 μm , while that of the latter is 7.18 μm . While successful laser action has been achieved with this system,¹¹⁹ it is now largely of historical importance. One of the difficulties with this scheme that is probably common to all systems involving high-lying electronic states is the relatively large cross sections that characterize collisions between highly excited systems. For example, Cummins¹²⁰ has estimated that the cross section for the excitation transfer process



is $250 \times 10^{-16} \text{ cm}^2$. Similarly, he estimates that the quenching cross sections for the $8^2S_{1/2}$ and $6^2D_{3/2}$ states by xenon are $85 \times 10^{-16} \text{ cm}^2$ and $4100 \times 10^{-16} \text{ cm}^2$, respectively. There is also the problem that narrowband pumping is required, but this may not be a serious objection of one utilizes a laser pump. As indicated above, the energy efficiency of this scheme is necessarily quite limited even though the quantum efficiency may be large.

More recently, Sorokin¹²¹ and coworkers have observed infrared laser action in alkali atoms formed by the photodissociation of alkali molecules with two-photon excitation utilizing pulsed lasers. Cesium, rubidium, and potassium have been found to oscillate when suitably irradiated. In the case of cesium, laser action occurs at 1.360 and 1.376 μm in the absence of helium buffer gas, and at 3.095 and 3.050 μm in the presence of about an atmosphere of helium. The short wavelengths correspond to the 7p-5d atomic transitions, while the longer wavelengths correspond to the 7p-7s transitions. In both cases, pumping of the cesium dimer is accomplished with a pulsed ruby laser. The laser output power is found to vary as the

square of the pumping power, as expected, for a two-photon excitation process. The excitation involves a two-photon transition from the $1\Sigma_g^+$ ground state of the alkali dimer to a dissociating state that produces the upper level of the atomic system. Virtual intermediate transitions are made to the $1\Pi_u$ dimer band. An important part of the experimental work involved the development of heat-pipe cells for creating a large dimer concentration. This technology may have other important applications in laser research and developments.

High pulse powers of $1.315\ \mu\text{m}$ have been obtained from iodine atoms excited to the $2P_{1/2}$ state by photolysis of RI molecules where R can be CH_3 , CF_3 , C_3F_7 , and similar species.¹²² The prototype of this reaction is the photolysis of I_2 in which it is well known that one atom comes out in the excited $2P_{1/2}$ state and the other in the $2P_{3/2}$ ground state. The photolysis of RI proceeds by the electronic excitation of RI to an autodissociating state that leaves the I in the excited $2P_{1/2}$ level. Peak powers of 1.2 GW have been achieved with this system. Presumably, similar systems can be found for other halogen atoms, but the $2P_{1/2} - 2P_{3/2}$ laser wavelength would increase rapidly with decreasing halogen weight. In the case of bromine, the laser wavelength would be $2.72\ \mu\text{m}$, and the pump wavelength would be about $2200\ \text{\AA}$, an overall situation less favorable than that for iodine. Since the iodine system requires an ultraviolet ($2700\ \text{\AA}$) pump and yields a $1.3\text{-}\mu\text{m}$ laser beam, the energy efficiency is not high, but as noted above, the peak power is very high and an energy of 65 J per pulse has been achieved. This system is scalable to very high pulse energies and is one of the candidate systems for laser fusion.

The examples given above indicate the diversity of systems in which infrared laser action occurs between close-lying, highly excited states. Many other examples can be found in the literature. A possible candidate for inclusion in this list is the exploding-wire laser in which a metallic

wire is exploded in an oxidizing atmosphere.¹²³ Strong infrared laser action is found in a large number of such systems. It is not known with certainty whether the laser levels involve the metal atoms, the product oxide molecule, or molecular ions. In the case of the aluminum fluoride exploding-wire laser, Rice and Jensen believe that the laser action in the spectral region from 12.5 to 13.5 μm occurs between vibrational and rotational levels in the ground electronic state of AlF .¹²³ A number of other exploding-wire lasers have been reported by Rice and Beattie.¹²⁴ Clearly a large amount of work must be done to understand and optimize these exotic systems.

Appendix C

SUMMARY OF SCHEDULED PRESENTATIONS

Appendix C

SUMMARY OF SCHEDULED PRESENTATIONS

A summary of the scheduled presentations heard at the 1975 JASON Winter Infrared Laser and Reaction Rate Study is given below.

<u>Participant (Affiliation)</u>	<u>Topic</u>	<u>Date</u>
T. Y. Chang (BTL)	Far Infrared on Optically Pumped Lasers	1/7/75
H. Fetterman (MIT/LL)	Off-Resonant Optical Excitation and Stark Tuning	1/7/75
T. Deutsch (MIT/LL)	Optically Excited Energy Transfer Systems	1/7/75
R. Prasad (AFCRL) C. Leiby (AFCRL)	Plasma Generated Far Infrared Radiation	1/7/75
R. Airey (NRL)	Laser Chemistry	1/7/75
R. Zare (Columbia)	Laser Chemistry	1/7/75
D. Brabson (AFWL)	AFWL Laser Program	1/9/75
<u>Other Visitors* (Affiliation)</u>		<u>Date</u>
G. Flynn (Columbia)		1/7,8/75
A. Szoke (JILA)		1/7/75

* No explicit presentation given.

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ATTN: Dr. John Asmus

Mr. Lawrence Peckham
Science Applications, Inc.
1911 N. Ft. Myer Drive, Suite 1200
Arlington, VA 22209

Science Applications, Inc.
P.O. Box 328
Ann Arbor, MI 48103
ATTN: Dr. R. E. Meredith

Science Applications, Inc.
6 Preston Court
Bedford, MA 01730
ATTN: Dr. Robert Greenberg

Systems Consultants, Inc.
1050 31st St., N.W.
Washington, D. C. 20007
ATTN: Dr. Robert B. Keller

Systems, Science and Software
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LaJolla, CA 92037
ATTN: Mr. Alan F. Klein

Thiokol Chemical Co.
WASATCH DIVISION
P.O. Box 524
Brigham City, UT 84302
ATTN: Mr. James E. Hansen

TRW Systems Group
One Space Park
Bldg. 01, RM 1050
Redondo Beach, CA 90278
ATTN: Mr. Norman F. Campbell

United Aircraft Research Laboratory
400 Main St.
East Hartford, CONN 06108
ATTN: Mr. G. H. McLafferty
Mr. Albert Angelbeck

United Aircraft Corp.
Pratt and Whitney Acft. Div.
Florida R&D Center
West Palm Beach, FL 33402
ATTN: Dr. R. A. Schmidtke
Mr. Ed Pinsley

VARIAN Associates
EIMAC Div.
301 Industrial Way
San Carlos, CA 94070
ATTN: Mr. Jack Quinn

Vought Systems Div.
LTV Aerospace Corp.
P.O. Box 5907
Dallas, TX 75222
ATTN: Mr. F. G. Simpson
Mail Station 2-54142

Westinghouse Electric Corp.
Defense and Space Center
Friendship International Airport - Box 746
Baltimore, MD 21203
ATTN: Mr. W. F. List

Westinghouse Research Laboratory
Beulah Rd., Churchill Boro.
Pittsburgh, PA 15235
ATTN: Dr. E. P. Riedel
Mr. R. L. Hundstad

National Bureau of Standards
Boulder, Colorado 80303
ATTN: Dr. Earl Smith
Dr. Merrill Hessel

Dr. Arthur O. McCoubrey
Department of Commerce
National Bureau of Standards
Washington, D. C. 20234

Dr. W. S. Lewellen
Aeronautical Research Associates
of Princeton, Inc.
50 Washington Road
Princeton, New Jersey 08540

Dr. Steven N. Suchard
Aerospace Corporation
2350 E. El Segundo Blvd.
El Segundo, CA 90245

Dr. R. Zare
Department of Chemistry
Havemeyer Hall
Box 308
Columbia University
New York, NY 10027

Dr. George W. Flynn
Department of Chemistry
315 Havemeyer Hall
Columbia University
New York, NY 10027

Dr. N. Bloembergen
Gordon McKay Laboratory
Harvard University
Cambridge, MASS. 02138

Dr. Paul Kelley
MIT/Lincoln Laboratories
Lexington, MASS. 02173

Dr. Jeffrey I. Steinfeld
MIT
Department of Chemistry
Room 2-221
Cambridge, MASS. 02139

Dr. Richard Temkin
MIT National Magnet Laboratory
190 Albany St.
Cambridge, MASS. 02139

Dr. E. V. George
MIT
Cambridge, MASS. 02139

Dr. A. Szoke
MIT
Department of Electrical Engineering
Cambridge, MASS. 02139

Dr. A. Mooradian
MIT/Lincoln Laboratories
Lexington, MASS. 02173

Dr. R. Osgood
MIT/Lincoln Laboratories
Lexington, MASS. 02173

Mr. H. W. Hendel
Princeton University
P.O. Box 710
Princeton, NJ 08540

SA1
1651 Old Meadow Rd.
Suite 620
McLean, VA 222101
ATTN: Dr. Walter R. Sooy
Dr. R.M. Dowe, Jr.

Dr. Arthur L. Schawlow
Varian Bldg., Room 108
Department of Physics
Stanford University
Stanford, CA 94305

Dr. Stephen E. Harris
Hansen Labs-Microwave 37
Stanford University
Stanford, CA 94305

Dr. Arlan O. Scully
Department of Physics
University of Arizona
Tucson, Arizona 85721

Dr. Herbert P. Broida
Chemistry Department
University of California
Santa Barbara, CA 93106

Dr. John Cooper
Joint Institute for Laboratory Astrophysics
University of Colorado
Boulder, Colo. 80302

Dr. John Marburger
Department of Physics
University of Southern California
University Park
Los Angeles, CA 90007

Prof. D. R. Herschbach
Chemistry Department
Harvard University
Cambridge, MASS. 02138

Dr. Robert Center
AVCO-Everett Research Laboratories
2385 Revere Beach Parkway
Everett, MASS. 02149

Office of Naval Research
800 N. Quincey St.
Arlington, VA 22217
ATTN: Dr. Wm. J. Condell

H. C. Volkin, L-5
Los Alamos Scientific Laboratory
P.O. Box 1663
Los Alamos, NM 87544

Polytechnic Institute of New York
Route 110
Farmingdale, NY 11735
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Stanford Research Institute
333 Ravenswood Ave.
Menlo Park, CA 94025
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R. D. Hake N. Cianos
D. C. Lorents
F. T. Smith
R. C. Honey
K. S. Krishnan
R. Yadavalli
G. Langford
R. Marth
C. K. Rhodes
D. L. Huestis

Dr. David O. Harris
University of California
Santa Barbara, CA 93106

Dr. James E. Bayfield
Physics Department
Yale University
New Haven, CT 06520

Dr. C. Frederick Hansen
NASA/Ames Research Center
Moffett Field, CA 94035

D. Tompkins
Physics Department
University of Wyoming
Laramie, Wyoming 82070

Jerry Vigil
W. J. Schafer Associates, Inc.
14 Lakeside Office Park
Wakefield, MA 01880

Dr. T. K. Tio
Laser and Gas Dynamics Laboratory
UCSD, P.O. Box 109
La Jolla, CA 92037

NASA-Lewis Research Center
Cleveland, OH 44135
ATTN: Library

W. K. Schuebel
AFAL/DHO-1
Wright-Patterson AFB, OH 45433

J. A. Haberman
Box 99
Baker Laboratory of Chemistry
Cornell University
Ithaca, NY 14853

Okitsugu Kajimoto
Department of Chemistry
Faculty of Engineering Science
Osaka University
Toyonaka, Osaka 560, Japan

W. Weitzen
KMS Industries
1747 Pennsylvania Ave. NW
Washington, DC 20006

Joshua H. Rosenbloom
Air Force Office of Scientific Research/NE
Bldg. 410
Bolling AFB
Washington, DC 20332

Dr. John Madey
Hansen Laboratories
Stanford, California 94305

Prof. William Louisell
University of Southern California
Los Angeles, CA 90007