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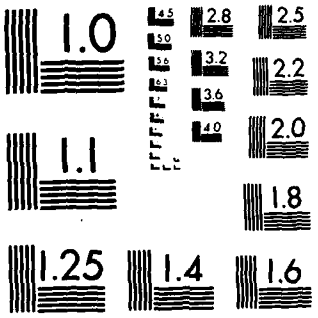

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER ARO 18105.8-PH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE *(and Subtitle)* Interaction of High Intensity Subnanosecond CO_2 Laser Pulses with Molecules		5. TYPE OF REPORT & PERIOD COVERED Final Report, for period April 13, 1981-April 12, 1984
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) N. Bloembergen		8. CONTRACT OR GRANT NUMBER(s) DAAG-29-81-K-0071
9. PERFORMING ORGANIZATION NAME AND ADDRESS Harvard University, Division of Applied Sciences, Pierce Hall, Cambridge, MA 02138		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
ONTROLLING OFFICE NAME AND ADDRESS J. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE June 1984
		13. NUMBER OF PAGES 4
IONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

DISTRIBUTION STATEMENT *(of this Report)*

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17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

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18. SUPPLEMENTARY NOTES

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19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

- collisionless infrared multiphoton excitation
- intramolecular vibrational energy redistribution
- picosecond resolution

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The purpose of the research performed under this contract was to eliminate the influence of collisions on the infrared multiphoton excitation of polyatomic molecules as much as possible, and to study the exchange and distribution of energy within an isolated polyatomic molecule. Extremely rapid equilibration of absorbed energy among the different modes was observed. New experiments involving time-resolved Raman spectroscopy of infrared multiphoton-excited molecules have, for the first time, provided more direct, quantitative information on intramolecular energy transfer.

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ARO 18105.8-PH

U.S. ARMY RESEARCH OFFICE

FINAL REPORT

1. ARO PROPOSAL NUMBER: P-18105-P

2. PERIOD COVERED BY REPORT: April 13, 1981 - April 12, 1984

3. TITLE OF PROPOSAL: Interaction of High Intensity Subnanosecond CO_2 Laser Pulses with Molecules.

4. CONTRACT OR GRANT NUMBER: DAAG29-81-K-0071

5. NAME OF INSTITUTION: Harvard University, Division of Applied Sciences
Cambridge, MA 02138

6. AUTHOR OF REPORT: N. Bloembergen

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7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP DURING THIS PERIOD, INCLUDING JOURNAL REFERENCES:

R.C. Sharp, E. Yablonovitch and N. Bloembergen, "Picosecond infrared double resonance studies on pentafluorobenzene", J. Chem. Phys. 76, 2147 (1982).

J.Y. Tsao, T.B. Simpson, N. Bloembergen and I. Burak, "The dynamics of infrared multiphoton pumping of optically excited NO_2 molecules", J. Chem. Phys. 77, 1274 (1982).

T.B. Simpson, J.Y. Tsao, I. Burak and N. Bloembergen, "The dynamics of infrared multiphoton pumping of excited NO_2 molecules", summary of paper presented at the 12th International Conference on Quantum Electronics, Appl. Phys. (Springer) B 28, 181 (1982).

T.B. Simpson, E. Mazur, I. Burak, N. Bloembergen and K.K. Lehmann, "Infrared multiphoton excitation of DN_3", J. Chem. Phys. 79, 3373 (1983).

R.C. Sharp, E. Yablonovitch and N. Bloembergen, "Infrared double resonance studies of intramolecular energy transfer", title of paper presented at the Third Topical Meeting on Picosecond Phenomena, Garmisch-Partenkirchen, June 1982, Appl. Phys. B 28, 314 (1982).

T.B. Simpson and N. Bloembergen, "Infrared multiphoton excitation of SO_2 to fluorescent states", Chem. Phys. Lett. 100, 325 (1983).

N. Bloembergen, I. Burak and T.B. Simpson, "Infrared multiphoton excitation of small molecules", invited paper presented at the EUCMOS XVI Conference in Sofia, Bulgaria, September 1984, J. Mol. Struct. 113, 69 (1984).

N. Bloembergen, I. Burak, E. Mazur and T.B. Simpson, "Infrared multiphoton excitation of small molecules", Israel J. Chem. (1984)

E. Mazur, I. Burak and N. Bloembergen, "Collisionless vibrational energy redistribution between infrared and Raman active modes in SF_6", Chem. Phys. Lett. 105, 258 (1984).

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E. Mazur, I. Burak and N. Bloembergen, "Time-resolved Raman spectroscopy of infrared multiphoton excited molecules", paper to be presented at XIII International Conference on Quantum Electronics, June 1984, Anaheim, Calif., summary in J. Opt. Soc. Am. B: Optical Physics 1, 538-539 (1984).

T.B. Simpson and N. Bloembergen, "Infrared multiphoton dissociation of SO_2", paper to be presented at XIII International Conference on Quantum Electronics, June 1984, Anaheim, Calif., summary to be published in J. Opt. Soc. Am. B: Optical Physics (1984).

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:

Dr. Itamar Burak - July 1-October 31, 1981; July 1-November 15, 1982;
July 1-October 31, 1983.

Dr. Eric Mazur - January 1, 1982 - April 12, 1984

Dr. Richard C. Sharp - April 13, 1981 - June 30, 1982

Dr. Thomas B. Simpson - April 13, 1981 - August 15, 1983

Dr. Jeff Y. Tsao - April 13 - September 30, 1981

Mr. Jeff Tsao was awarded the Ph.D. degree in Applied Physics from Harvard University in October 1981. The title of his Ph.D. thesis is: "The infrared multiphoton pumping of molecules in excited electronic states".

Mr. Richard C. Sharp was awarded the Ph.D. degree in Chemical Physics from Harvard University in June 1982. The title of his Ph.D. thesis is: "Picosecond time resolved studies of sulfur hexafluoride and pentafluorobenzene".

Mr. Thomas B. Simpson was awarded the Ph.D. degree in Applied Physics from Harvard University in August 1983. The title of his Ph.D. thesis is: "Infrared multiphoton excitation of small polyatomic molecules".

9. OUTLINE OF PROBLEMS STUDIED AND SUMMARY OF THE MOST IMPORTANT RESULTS:

The purpose of the research performed under this contract was to eliminate the influence of collisions on the infrared multiphoton excitation of polyatomic molecules as much as possible, and to study the exchange and distribution of energy within an isolated polyatomic molecule.

The results are best summarized in four categories:

a. Collisionless Excitation and Dissociation of Small Molecules

In most previous work on the infrared multiphoton excitation of small molecules, the influence of collisions could not be ruled out. Experiments have now been completed for OCS, NO_2, NH_3, DN_3 and SO_2 with verified collisionless excitation, using the rather unique high-power picosecond CO_2 laser system developed at Harvard. The results show that there exists a gradual transition from the regime of discrete states in small molecules to the so-called quasi-continuum regime in large molecules, where the excitation shows a strict fluence dependence. For triatomic molecules it was found that most of the molecules remain unexcited, whereas a small fraction may be excited in a multiphoton process. The excitation is therefore predominantly determined by the intensity. For intermediate-size molecules, up to 10 atoms, both intensity and fluence play a role.

b. Infrared-Infrared Double Pulse Spectroscopy with Picosecond Resolution

Using two synchronized 50 ps pulses from two independently tunable CO_2 lasers, pump-probe experiments have been performed on pentafluorobenzene. This molecule has two infrared active modes which are accessible to the CO_2 laser wavelengths, and therefore allows a direct investigation of the intramolecular vibrational energy redistribution between different infrared modes. The results indicate an extremely rapid equilibration (< 50 ps) of absorbed energy among the two modes. The final distribution of energy, moreover, is consistent with thermal (statistical) heating.

c. Infrared Multiphoton Excitation of Optically Excited NO_2 Molecules

Although ground state NO_2 molecules do not interact with CO_2 laser radiation, optically excited NO_2 molecules do interact. The dynamics of infrared multiphoton excitation were studied systematically by varying the optical excitation energy and thereby the preparation of the molecule in a well-defined energy region (just) below the dissociation threshold. This has made possible the first direct observation of the final dissociative step in the excitation and also the first observation of stimulated infrared multiphoton emission processes. The results again show that intensity effects play an important role, except for the last dissociative transition, which obeys Fermi's Golden Rule very well. Estimates of the density of vibrational states are too low, however, to satisfy the conditions for a quasicontinuum. Apparently, rotational selection rules do not hold in the highly excited states, and the effective density of states may be several orders of magnitude higher than estimated, giving rise to the observed behavior.

d. Time-Resolved Raman Spectroscopy of Infrared Multiphoton Excited SF_6

Infrared multiphoton excitation followed by an intense ultraviolet light pulse provides a means of directly observing the transfer of vibrational excitation from infrared to Raman active modes. Detailed experiments have been performed for SF_6, opening the door to a more quantitative study of infrared multiphoton excitation and the physical understanding of intramolecular energy redistribution.

The results show that redistribution of energy occurs even under collisionless conditions. Comparison with photoacoustic results obtained earlier shows that (within experimental accuracy) there is equipartitioning among the various modes (intramolecular equilibrium). The redistribution of energy persists even at very low infrared fluence, when the average absorption per molecule is reported to be below one infrared photon. This indicates that the intermolecular distribution is far from equilibrium, with a few molecules being highly excited while the majority remains virtually unexcited. These recent experiments provide a new handle on the study of intramolecular dynamics.

J. Opt. Soc. Am. B: Optical Physics, Vol. 1, No. 3/June 1984/ pp. 538-539.

ing time T_2 of the $R(3)$ vibration–rotation transition of HCl is measured to be $T_2 \times p$ = 21.5 psec × bar in the pressure range p = 0.5 to 3 bar, in good agreement with spectroscopic data.[3] The theoretical predictions for $\alpha l < 1$ are verified studying HCl:Ar mixtures with a total pressure of 3 bar. Collective beating of two neighboring isotopic species ($C^{35}HI$ and $H^{37}Cl$) is directly observed for the first time known in coherent pulse propagation.[4] The measured beating period of 15.0 ± 0.3 psec is in excellent agreement with theoretical and spectroscopic numbers for the isotopic line splitting.

In summary, we show that quantitative information can be substracted from studies of coherent pulse propagation on the picosecond time scale. Small-area pulses are found to be particularly well suited because of the linear intensity dependence. The potential of the technique is elucidated. (12 min.)

[1] M. D Crisp, Phys. Rev. A 1, 1604 (1970).

[2] H. P. Grieneisen, J. Goldhar, N. A. Kurnit, A. Javan, and H. R. Schlossberg, Appl. Phys. Lett. 21, 559 (1972); S. M. Hamadani, J. Goldhar, N. A. Kurnit, and A. Javan, Appl. Phys. Lett. 25, 160 (1974).

[3] H.-J. Hartmann and A. Laubereau, Opt. Commun. 47, 117 (1983).

[4] H.-J. Hartmann, K. Bratengeier, and A. Laubereau, to be published.

ThCC4. Self-Transparency Effects in Nonlinear Light-Scattering Inhomogeneous Media and Their Possible Use in Lasers, G. B. Altshuler, V. S. Ermolaev, K. I. Krilov, A. A. Manenkov, and A. M. Prokhorov, *Academy of Sciences of the USSR, General Physics Institute, 117942 Moscow, Vavilov Street 38, USSR.*

Transmission of intense laser beams through heterogeneous scattering media is considered. The laser-induced transparency effects (suppression of scattering) in such media due to compensation of the linear refractive-index difference Δn_L of heterocomponents of a medium by nonlinear change Δn_{NL} for different mechanisms of nonlinearity are predicted and experimentally observed. Applications of these effects in lasers (for Q switching, mode locking, etc.) are discussed. (Invited paper, 25 min.)

Thursday, June 21, 1984
10:30 AM Orange County Ballroom

Molecular Dynamics

M. M. T. LOY, Presider

IBM T. J. Watson Research Center

ThDD1. Time-Resolved Raman Spectroscopy of Infrared Multiphoton Excited Molecules, E. Mazur, I. Burak,* and N. Bloembergen, *Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138.*

Previous investigations have shown that infrared multiphoton excited polyatomic molecules (re)distribute the absorbed infrared energy among their different vibrational degrees of freedom. Multiphoton excitation of an infrared mode therefore alters the excitation of other modes, including Raman-active modes. From the change in Raman signals one can thus obtain information on the intramolecular vibrational distribution produced by *infrared multiphoton excitation.*

A typical experimental result, obtained for SF_6 at 1 *Torr and room temperature, is shown* in Fig. ThDD1-1. The Stokes and anti-Stokes signals are measured relative to the *thermal Stokes signal and are plotted here as* a function of the delay between exciting infrared pulse and probing ultraviolet pulse. After an initial rise, which in this particular measurement is limited by the 18-nsec duration of the probe pulse, the signals remain constant. A similar behavior is observed over a large range of pressures (0.1 to 1 Torr), time scales (20 nsec to 4 µsec) and infrared laser fluences (0.02 to 1 J/cm²). Since the infrared excitation occurs under collisionless conditions (exciting pulse, 0.5 nsec), and the probing is performed in both collisional and collisionless regimes, the constant behavior indicates that collisionless infrared multiphoton excitation creates an intramolecular vibrational distribution close to thermal equilibrium.

In Fig. ThDD1-2 the dependence of the signals on the infrared laser fluence is shown for various pressures. The fact that there is no dependence on pressure is another indication that collisions do not alter the intramolecular distribution.

Small changes in Raman signal have been observed at infrared laser fluences as low as 0.015 J/cm², where the average absorption per molecule is known to be below one infrared photon per molecule. Since collisionless redistribution of energy can only occur at relatively high levels of excitation, this indicates that even at these very low fluences some molecules undergo multiphoton excitation, while others remain unexcited. Hence the intermolecular vibrational distribution differs significantly from an equilibrium distribution.

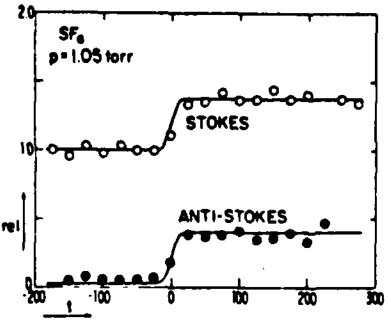

Fig. ThDD1-1. Intensity of Stokes and anti-Stokes signals as a function of the time delay t between pump and probe pulses, measured relative to the thermal Stokes signal. The average fluence of the infrared pump laser is 0.34 J/cm². The risetime in the curves reflects the 18-nsec FWHM duration of the probe pulse.

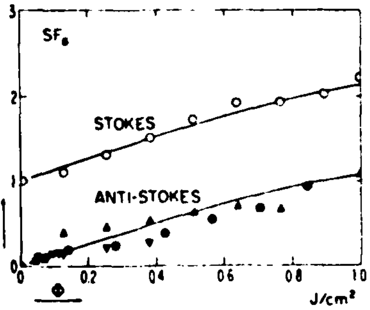

Fig. ThDD1-2. Relative Stokes (open symbols) and anti-Stokes (closed symbols) signals versus infrared laser fluence Φ for various pressures. ○●, 1.05 Torr; ■, 0.50 Torr; ▼, 0.52 Torr; ▲, 0.11 Torr.

From the ratio between Stokes and anti-Stokes signals one can furthermore determine the total energy stored in the Raman-active mode, which in turn can be compared with the energy in other modes, obtained in a similar way, and to the total amount of absorbed laser energy, known from photoacoustic measurements. Such a comparison has been carried out, and experimental results for several molecular systems are discussed. (12 min.)

* Permanent address: *Department of Chemistry, Tel Aviv University, Tel Aviv, Israel*

ThDD2. Determination of the H + D_2 Product State Distribution Using a Novel Laser Ionization Mass Spectrometer, E. E. Marinero and C. T. Rettner, *IBM Research Laboratory, Department K46/282, 5600 Cottle Road, San Jose, California 95193,* and R. N. Zare, *Department of Chemistry, Stanford University, Stanford, California 94305.*

The hydrogen atom exchange reaction $H + H_2 \rightarrow H_2 + H$ and its isotopic analogs are of fundamental importance to the field of chemical-reaction dynamics. However, this thermoneutral system has a large activation barrier and only a small reaction cross section. In addition, the reaction products are difficult to detect using standard laser techniques. These facts have until recently hindered efforts to determine the nascent quantum-state distributions for these reactions.

We report on a novel laser-based approach for studying these reactions and have obtained the state distribution for the HD product as well as detected nascent D atoms in the $H + D_2$ reaction at a collision energy of ~1.3 eV.

Our method comprises three important elements: (a) Fast H atoms are produced by

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