Laser-Induced Infrared Multiphoton Isomerization Reactions of 2,4- and **1.3-Hexadienes**

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Efficient and clean isomerization has been observed in the system consisting of the conjugated 2,4- and 1,3-hexadienes following infrared multiphoton excitation of these species. Variations of both laser fluence and pressure of added inert gas are seen to significantly effect branching ratios and yields. Where a competition exists between a low activation energy, low preexponential factor pathway and one with a high activation energy, high preexponential factor, an increase in fluence is seen to favor the latter pathway. An estimate of the degree of excitation in the molecule is obtainable from product branching ratios and inert gas quenching behavior. Photoacoustic measurements of energy input coupled with observation of product ratios indicate that the production of multiple products in a single laser pulse is compatible with a sequential isomerization mechanism which takes place in an almost vibrationally adiabatic fashion. Thermal and CW laser studies of hexadiene isomerization have been performed. Thermal studies yield rate constants and ΔH and ΔS for the various isomers. Thermal studies coupled with multiphoton studies have helped establish the isomerization pathway connecting the cis, trans-2,4- and trans-1,3-hexadiene isomers and have confirmed the other isomerization pathways in the system. The pathways for CW cw laser-induced isomerization have been studied.

Introduction

In the presence of intense infrared laser radiation, molecules may be vibrationally excited via the absorption of multiple photons and thus rendered capable of undergoing reaction. The absorption process is commonly referred to as multiphoton excitation (MPE) and has been widely studied since its discovery in the past decade. Much is already understood regarding the process and the general features of the phenomenon have been elaborated on in a number of recent publications.¹

An attribute of infrared MPE, one which has given it great promise in chemical studies, is its high frequency selectivity. Numerous examples exist in which the isotope effect on vibrational frequencies has been exploited to selectively excite and dissociate a specific isotopic species.¹⁻⁶ Similarly, it has been demonstrated that frequency shifts due to configurational differences may be utilized to effect excitation of specific isomers in an isomeric mixture.7-13

MPE-induced isomerization reactions are of interest for a variety of reasons. Isomerization reactions differ from dissociation reactions in that it is not necessary to excite molecules into the dissociative continuum for reactions to occur. Thus, isomerizing systems may well be a better probe of energy utilization and disposition in the quasi-continuum than other types of reactions. MPE also may represent a new means of producing thermodynamically disfavored isomers.^{15,16} In the case of multiple-component systems, product ratios from competing and consecutive reaction pathways can be studied as a function of experimental parameters.

In an earlier work, we described the isomerization of conjugated hexadienes, where it was possible through preferential excitation to modify the composition of an isomeric mixture to include a high percentage of thermally disfavored species. This was accomplished without significant loss of starting material which might occur due to competing fragmentation reactions.¹⁵ Certain features of this system suggested it as having further value as a probe of multiple-photon excitation and reaction mechanisms. Evidence for a fluence and pressure dependence of single-pulse product ratios suggested a means by which the dynamical factors governing the variation of product ratios in a multicomponent system could be probed. Since it has been generally observed that MPE-induced reactions proceed by pathways similar to those for thermally excited systems, a thorough understanding of the thermal kinetics and thermochemistry for the hexadiene system would be expected

to provide further basis for fuller comprehension of MPE-induced reactions in these systems.

We now report on experiments involving the variation of product ratios in the hexadiene system as a function of laser fluence and quenching gas pressure. RRKM calculations and absorption measurements have been coupled with the above studies to provide insight into isomerization dynamics. Thermal rate constants and relative thermodynamic stabilities have been obtained for several isomers where this data did not already exist in the literature. Thermal reaction pathways and the results of continuous wave (CW) CO₂ laser irradiation of sensitized samples have been compared to MPE pathways under a variety of conditions; all of the above is an effort to elucidate the factors that govern the dynamics of isomerization in the hexadienes.

Experimental Section

Starting Materials and Photochemical Enrichment of cis-1,3-Hexadiene. Hexadiene starting materials were purchased from Albany International. trans, trans-, cis, trans-, and cis, cis-2,4hexadiene were found to have a purity of greater than 99, 99, and 98%, respectively. Purities were determined by gas chromatography using columns to be discussed later and no attempt was made at further purification of these isomers. Principal impurities in each case were other hexadiene isomers. Corrections for im-

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purities in the starting material have been made in all reported results.

The 1,3-hexadienes were obtained as a mixture of cis and trans isomers which varied in composition from batch to batch. In some cases the cis isomer comprised only a small percentage of the mixture and the percentage had to be increased before the isomers were separated by preparative gas chromatography. Enrichment in cis isomer was accomplished by preparative photochemical isomerization.¹⁷ A solution, 0.2 M in 1,3-hexadiene and 0.03 M in benzophenone, in n-pentane (Aldrich, spectrochemical grade) was irradiated with a Hanovia medium-pressure mercury lamp equipped with a Pyrex lampwell. A steady-state concentration of 38% cis-1,3-hexadiene was established after 2 h of irradiation. The bulk of the solvent was then removed by distillation through a column packed with glass beads. When the temperature at the column head began to rise from that corresponding to the boiling point of pentane, the distillation was terminated. The residue was then injected in 250-µL aliquots into a preparative gas chromatograph using a 15 ft $\times 1/4$ in. column packed with a 1:3 mixture of saturated AgNO₃ solution in benzyl cyanide on 40/60 mesh C-22 firebrick. Helium carrier gas flow was 75 scm³/min with products collected in a dry ice cooled vessel by means of a 10:1 effluent splitter. After separation, both the trans and cis isomer were analyzed by gas chromatography (GC) and found to be >99% pure.

Thermal Rate and Equilibrium Measurements. Thermal rate constants and thermodynamic equilibria were measured via standard techniques described in a variety of references.¹⁸ Reactions were run in a 1-L Pyrex bulb enclosed in a Lindberg tube furnace. The ends of the tube furnace were packed with glass wool. Temperatures as measured by a thermocouple varied by less than 1% during a typical run. The temperature was found to be uniform throughout the volume occupied by the reaction vessel. The bulb was centered in the furnace and connected by a glass capillary to a Kontes teflon valve situated immediately at the exterior of the furnace. This valve in turn was coupled to a vacuum line used for sample handling, to which was attached a 50-mL Pyrex bulb used for product collection. For kinetic measurements, the bulb in the furnace was conditioned overnight at reaction temperatures by using 5 torr of starting material. The material was pumped out and the bulb filled by expansion with 5 torr of new material. Reactions were terminated by expansion of products into the oscillator vessel which was previously evacuated and at room temperature. The temperature ranges used were 190-270 °C for trans-1,3-hexadiene, 315-415 °C for trans, trans-2,4-hexadiene, and 280-350 °C for cis, cis-2,4-hexadiene. All reactions produced cis, trans-2,4-hexadiene as the primary product after a typical reaction time of 1 h. As a check, a number of rate measurements were run in a conditioned 50-mL Pyrex bulb equipped with a teflon valve. The bulb was immersed in a stirred $KNO_3/NaNO_2$ eutectic bath. In this case, reactions were terminated by rapid immersion of the bulb in cold water. The eutectic bath apparatus gave identical results over the same temperature and pressure ranges used with the tube furnace; however, the latter was deemed preferable due to the larger reaction vessel that could be used, the broader temperature range available, and greater reliability for runs of long duration.

Thermal equilibria were established by a similar procedure over a temperature range of 350-450 °C. Equilibrium was considered established when product ratios as measured by GC did not change with time. This generally required from a few hours to several days depending on temperature. Results were checked by using several different initial isomers.

Laser Experiments. Unless otherwise stated, all MPE and CW irradiation experiments were performed by using 0.1 torr of

hexadiene starting materials in a $10 \text{ cm} \times 20 \text{ mm}$ diameter Pyrex cell. The cells were equipped with teflon valves and closed with "O" ring sealed, clamped NaCl windows.

MPE experiments employed either of two lasers. One was a homemade double discharge Rogowski profile TEA laser with an output pulse which consisted of a 60-ns spike (fwhm) containing approximately 50% of the pulse energy which was followed by a ~600-ns (fw) tail. Fluences for this laser varied from 0.8 to 2.2 J/cm² for an unfocused beam, depending on the line used. The beam from this laser was weakly focused by a 30-cm focal length lens placed 7 cm from the entrance window of the cell. This resulted in an average fluence at the center of the cell equal to 2.75 times the value for the unfocused beam. This laser was used for experiments not involving systematic variation of fluences.

For determination of the fluence dependence of product ratios, a Lumonics K203-2 CO₂ TEA laser was employed. Its pulse consisted of a 100-ns (fwhm) spike containing ~60% of the energy, followed by a ~1000-ns (fw) tail. The output beam was spatially filtered and directed into a Gallilean telescope. Variation of telescope optics allowed output fluences to be varied from 1.5 to 7 J/cm² for an input beam of ~2 J/cm². For both lasers, laser lines were determined with an Optical Engineering CO₂ laser spectrum analyzer, energies via a Scientech calorimeter, and pulse profiles with a photon drag detector. The lasers were operated on R(18) of the 10.6- μ m laser branch for all irradiations except those of *cis,cis*-2,4-hexadiene, and on P(38) of the 10.6- μ m branch for irradiation of that species.

The effects of varying pressure of collision partners on overall yield and branching ratios were investigated. Collision partners were either N_2 , Ne, or Ar for pressures up to 20 torr. These gases were Matheson research grade.

For experiments involving CW irradiation, samples were mixed with 1 torr of SF₆ and irradiated by the output of a longitudinally pumped, grating tuned, chopped CO₂ laser operating on the P(28) line of the 10.6- μ m laser branch. Typical output powers were 10 W and irradiation times were 60 s.

All volatile products in all types of experiments were characterized at least once by GC/mass spectrometry with comparisons being made to pure starting materials. A Hewlett-Packard 5985 mass spectrometer was employed.

Routine product characterization was done with a Varian 3700 FID gas chromatograph equipped with a gas sampling valve. The GC was operated at room temperature by using either of two columns. The first was a 20 ft \times ¹/₈ in. column packed with 20% 3,3'-dicyanoethyl ether on 80/100 mesh chromosorb P. This column gave excellent resolution of 2,4-hexadiene isomers but only partial resolution of 1,3-hexadienes. When additional resolution of 1,3 isomers was required, this column was followed by a 12-in. column packed with 25% saturated AgNO₃/benzyl cyanide solution on 60/80 mesh C-22 firebrick. Carrier flow was 300 scm³/min and the flame ionization detector temperature was 300 °C.

Absorption Measurements. A nonresonant optoacoustic cell was constructed of brass, had a total path length of 23 cm, and an outer diameter of 5 cm and was fitted with BaF2 windows which were sealed with viton O rings and clamped. An electret microphone (Knowles Electronics, Inc., Model BT-1759; bias, 1.3 V; sensitivity, $1 \text{ mV}/\mu \text{bar}$) was positioned at the center of the cell, 1 cm from the longitudinal cell axis. Cylindrical constrictions of 2 cm diameter, 3 cm length, located 5 cm from either end of the cell isolated the microphone from background noise due to window absorption. Signals were fed directly into an oscilloscope. No background signal was observed at any fluences when the cell was empty. Addition of 200 torr of either argon or neon to an empty cell produced a small signal at high fluences of different shape than that originating from absorption by the hexadienes and of intensity less than 0.1% of a typical hexadiene signal. It was concluded that background contributions to measured signals were negligible. Measurements were made of the peak-to-trough amplitude of the first acoustic wave following the laser pulse. Calorimetric determinations of adsorbed energy were made with a Scientech volumn absorbing calorimeter.

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Figure 1. Calculated RRKM rate constants, in units of s⁻¹, for the isomerization of cis, trans-2, 4-hexadiene to (a) cis-1, 3-hexadiene, (b) trans-1,3-hexadiene, (c) cis, cis-2,4-hexadiene, (d) trans, trans-2,4-hexadiene.

RRKM Rate Constants. RRKM rate constants for the isomerization of cis, trans-2,4-hexadiene to the other 2,4 and 1,3 isomers were calculated with the program by Hase and Bunker available through the Quantum Chemistry Program Exchange.²⁰ Rate constants were calculated incrementally for molecules in states above the isomerization barrier with each successive increment corresponding to an additional CO₂ photon energy. Vibrational frequencies for cis, trans-2, 4-hexadiene were obtained from published spectra and by comparison with frequencies for similar molecules.²¹ These data were supplemented by recording the Raman spectrum of the molecule.²² Frequencies and the conformation of the transition state were arrived at via comparison with previous calculations, 23,24 use of bond energy-bond order correlations, 25 and intuition. For cis-to-trans isomerization a reaction coordinate of 1000 cm⁻¹ was employed based on previous work.^{21e} For sigmatropic rearrangements, the reaction coordinate was chosen to be 2990 cm⁻¹ which corresponded to a C-H stretch.^{21b} The validity of calculated rate constants was judged by comparison with measured thermal rates. This was accomplished by summing the population-weighted state-specific RRKM

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Figure 2. Arrhenius plot for thermal isomerization of trans, trans-2,4hexadiene \rightarrow cis,trans-2,4-hexadiene. The plotted rate on the ordinate is in units of s⁻¹.

TABLE I: Measured Rate Parameters for Thermal Isomerization of Hexadienes

reaction	intercept, s ⁻¹	slope, kcal/mol
$trans, trans- \rightarrow cis, trans-2, 4$ -hexadiene	1.1×10^{13}	53.2 ± 2
$cis, cis \rightarrow cis, trans - 2, 4$ -hexadiene	8.3×10^{13}	49.6 ± 3
trans-1,3- \rightarrow cis, trans-2,4-hexadiene	1.2×10^{12}	41.0 ± 5
$cis-1,3- \rightarrow cis, trans-2,4$ -hexadiene	$6.3 imes 10^{10}$	32.5 (ref 32)

rate constants. The weighting factor was a Boltzmann distribution at a given temperature. This procedure was repeated for various temperatures and an Arrhenius A factor determined which was compared to the thermally determined A factor. Agreement was taken to indicate the validity of the calculated results which are summarized in Figure 1.

Results

Thermal Rate and Equilibrium Measurements. Data for the thermal isomerization of trans, trans-2,4-hexadiene are presented in Figure 2 as an Arrhenius plot of the logarithm of the measured rate constants vs. 1/T. The major product was cis, trans-2,4hexadiene, with traces of the trans-1,3 and cis,cis isomers occurring at higher temperatures and longer run times. No appreciable formation of cis-1,3-hexadiene was observed. Similar plots were made for the reactions of trans-1,3-hexadiene and cis,cis-2,4hexadiene. In the latter two cases, the products were cis, trans-2,4-hexadiene, together with some cis-1,3-hexadiene, which for cis, cis parent was assumed to occur through subsequent reaction of the cis, trans product.

All of the reactions studied manifested first-order behavior, although careful conditioning of the reaction vessel had to be undertaken to eliminate competitive surface reactions. The reactions were clean under the conditions studied as was evidenced by the absence of lighter fragmentation products and by the reproducible nature of results in a variety of vessels. Experimentally measured rate parameters determined from Arrhenius plots are shown in Table I.

Even though the reactions studied are reversible, as long as the rate constants are determined for a situation where the concentration of product at t = 0 is zero and the reaction has progressed a sufficiently small amount that the product concentration divided by the concentration of the product at equilibrium is << 1, the forward rate constant can be determined via the normal procedure for a first-order reaction.²⁶ These conditions were in effect for the reported experiments and thus the slopes and intercepts reported in Figure 1 can be viewed as the Arrhenius parameters for rate constants for the forward direction of the cited reactions.

The determination of ΔH and ΔS between the various hexadiene isomers required the measurement of equilibrium ratios of the

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TABLE II: Experimental and Calculated Equilibrium Parameters for Isomerization of cis, trans-2,4-Hexadiene

	ΔH , kcal/mol			ΔS , eu				
reaction	expt	caled 298 K	caled 650 K	ret 27 ^a	expt	caled 298 K	caled 650 K	ref 27 ^a
cis, trans. → trans, trans-2,4-hexadiene	-1.10	-1.00	-0.67	-0.86	-1.56	-2.40	-0.45	-1.4
cis,trans- → cis,cis-2,4-hexadiene	0.84	1.00	0.69	1.70	1.33	1.20	0.44	1.7
cis, trans-2, $4 \rightarrow$ trans-1, 3-hexadiene	3.26	1.94	2.43		-1.58	-2.55	-1.45	
$cis, trans-2, 4 \rightarrow cis-1, 3$ -hexadiene	3.48	2.94	3.11		-1.48	-1.35	-1.01	

^a Reactions were run over the temperature range 293-343 K.

TABLE III: Single-Pulse Yields^c

parent	% parent converted to products							
	trans, trans- 2,4	cis,trans- 2,4	<i>cis,cis-</i> 2,4	<i>trans</i> - 1,3	<i>cis</i> - 1,3			
trans, trans-2,4ª		1.53	0.33	0.61	0.78			
cis, trans-2,4 ^a	0.26		0.24	0.18	1.35			
cis,cis-2,4 ^a	0.00	0.00		0.00	0.00			
trans-1,3 ^a	0.00	0.20	0.09		0.24			
cis-1,3 ^a	0.06	1.11	0.08	0.47				
cis,cis-2,4 ^b	0.03	0.20		0.00	0.06			

^a R(18), 10.6- μ m irradiation. Fluence ~3.5 J/cm². ^b P(38), 10.6- μ m irradiation. Fluence ~2.5 J/cm². ^c The typical standard deviation for a given product yield was 15% of the yield. Irradiation used the loose focus geometry. Fluences at center of the cell are cited.

isomers in high temperature mixtures. Reliable estimates were complicated by thermal breakdown of the isomers at the temperatures necessary to drive the high barrier reactions to equilibrium. Results of these measurements are presented in Table II together with the numbers published by Doering for the iodine-catalyzed isomerization of the 2,4-hexadienes²⁷ and estimates achieved through group additivity calculations.²⁸ The latter were calculated for reactions run at room temperature and at 650 K. The 650 K calculations were performed to determine whether there were significant changes in ΔH and/or ΔS at elevated temperatures in a temperature regime similar to that for which equilibrium measurements were performed.

Pulsed Laser Experiments. Pulsed laser experiments were performed on pure samples with and without the addition of either nitrogen, neon, or argon as a collisions partner. The results of single-pulse experiments using the partially focused beam of the homemade CO_2 TEA laser are recorded in Table III. In addition to results published earlier,^{4a} it was possible to resolve both of the 1,3-hexadiene isomers and to investigate reactions when either isomer was used as a starting material. As can be seen, for all isomers under the specified conditions, the formation of multiple products is observed even after a single laser pulse. Since single-step thermal reaction pathways of these isomers yield a single product, this observation prompted an investigation of the mechanism of multiple product production.

To this end, a distinction was made for each starting material between the higher yield "primary" product, which coincided with that expected on the basis of single-step thermochemical kinetics, and the lower yield "secondary" products, which did not represent the reaction channel corresponding to a single step in a thermally excited system. The formation of secondary products could be explained by one of several mechanisms to be discussed in the next section. As an example, it was necessary to account for the presence of *cis,cis*-2,4-hexadiene was irradiated, since bulb experiments had demonstrated the single-step product to be *cis, trans*-2,4-hexadiene. Insight into the mechanism of single-pulse production of secondary isomers was achieved via a study of the single-pulse product ratios in systems in which fluence or quenching gas pressure was varied.





Figure 3. Variation of single-pulse product yield with neon pressure for cis, trans-2, 4-hexadiene irradiated with the R(18) line of the 10.6- μ m laser branch. Measurements were made in the loose focus geometry with a fluence of ~3.5 J/cm² at the center of the cell. The left-hand ordinate refers to cis-1, 3-hexadiene while the right-hand ordinate refers to the yield of all other products. Products are (\Box) cis-1, 3-hexadiene, (\blacktriangle) trans-1, 3-hexadiene, (\bigcirc) trans, trans-2, 4-hexadiene, and (\blacksquare) trans-1, 3-hexadiene.

In Figure 3 the dependence of product yield on rare gas pressure is illustrated for the case in which cis,trans-2,4-hexadiene/neon mixtures were subjected to pulsed laser radiation. Formation of *trans*-1,3- and cis,cis-2,4-hexadienes was virtually eliminated by the addition of 2.5 torr of rare gas. At a neon pressure of 5 torr, even cis-1,3-hexadiene, the product of the low activation energy channel available to cis,trans-2,4-hexadiene, was barely detectable. Similar results were obtained when N₂ was the collision partner, indicating that the extra internal degrees of freedom present in N₂ had little effect on its collisional quenching efficiency vs. a similar mass noble gas, Ne.

As shown in ref 29, even in a system in which the primary product was a high barrier product and a secondary product could occur via a subsequent low barrier process, the products could be almost exclusively limited to the first high barrier step by addition of rare gas. Along these lines and in an effort to verify the proposed thermal pathway for the isomerization of *trans*-1,3-hexadiene, this compound was irradiated and its product yield was studied as a function of added rare gas (Figure 4).

In a related experiment, the effect of increasing laser fluence was found to increase the fraction of high activation energy, high A factor products. This was most markedly the case for *cis*,-

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Figure 4. Variation of single-pulse product yield for *trans*-1,3-hexadiene irradiated at 3.5 J/cm^2 with a collimated beam on the R(18) 10.6- μ m CO₂ laser line. Product yields are given on the left-hand ordinate for the products: (\Box) *cis*-1,3-hexadine, (\blacktriangle) *cis*,*cis*-2,4-hexadiene, (\bigcirc) *trans*-2,4-hexadiene, and (\bigtriangleup) *cis*,*trans*-2,4-hexadiene. The right-hand ordinate indicates the ratio of *cis*-1,3-hexadiene to other products (\bigcirc) as a function of argon pressure.

cis-2,4-hexadiene vs. cis-1,3-hexadiene formation upon irradiation of cis,trans-2,4-hexadiene with collimated radiation of the R(18) line, 10.6- μ m branch from the Lumonics 203 TEA laser. trans-1,3-Hexadiene and trans,trans-2,4-hexadiene were also observed to comprise increasing fractions of the products at increasing fluences (Figure 5).

Absorption Measurements. Calorimetric measurements of the degree to which several of the hexadiene isomers absorbed laser radiation were performed in order to determine the average number of protons absorbed under reaction conditions. By observation of the change in absorbed laser energy which accompanied variation of pressure in a gas cell, it was possible to determine the average number of photons absorbed by a single molecule. For cis, trans-2,4-hexadiene, for the conditions under which most of the reactions were performed (a fluence of 3.5-4.0 J/cm^2), the average number of photons absorbed was 10 ± 2 . This number corresponds to the peak in the energy distribution of excited molecules, or about 30 kcal/mol for the absorption of 10 photons. However, most of the reacting molecules must be in the tail of the distribution of excited molecules with energies well removed from the average since 30 kcal/mol is below the lowest reaction barrier.

CW Irradiation. For comparison of multiple-photon reactions with those of a CW laser heated system, the results of laser driven reactions of SF₆-sensitized samples were determined.³⁰ In each case, when the system was irradiated with a $\sim\!10\text{-W}$ CW laser operating on the P(28) line of the 10.6- μ m CO₂ laser transition, mixtures of products were observed, even after an irradiation time of seconds. However, all product distributions were found to be consistent with those expected from thermochemical considerations. It was not possible to produce disfavored species such as cis, cis-2,4-hexadiene in nonequilibrium ratios. Average temperatures in the cell tended to be moderately high. For example, on the basis of rate data and extent of conversion of cis-1,3hexadiene to cis, trans-2,4-hexadiene, a temperature of 635 K was estimated. After 1 min, $\sim 25\%$ of parent was converted to product. Because of this high conversion of parent, it is possible that at least partial equilibrium was established between the isomers. If so, the average temperature could be even higher than the estimated value.

Discussion

Thermodynamic Parameters. The values determined for enthalpy and entropy changes for the reactions of the hexadienes are in qualitative agreement with both the values established by Doering²¹ and those predicted through group additivity calculations



Figure 5. Fractional single-pulse product yield as a function of R(18) 10.6- μ m laser fluence. The parent species is *cis,trans*-2,4-hexadiene. Product species are (**D**) *cis*-1,3-hexadine, (**A**) *cis,cis*-2,4-hexadiene, (**O**) *trans,trans*-2,4-hexadiene, and (**D**) *trans*-1,3-hexadiene. The indicated lines have been drawn to emphasize the trends for product yield vs. fluence.

of standard entropies and heats of formation (Table II).28 However, a few notable differences do occur. Doering observed little or no formation of 1,3-hexadienes, which may be ascribed to the fact that his experiments were performed at moderate temperatures and catalyzed by iodine which would not be expected to augment the 1,5 sigmatropic rearrangement.^{28,31} Additionally, in experiments reported on herein substantially less cis, cis-2,4hexadiene was observed in any equilibrium mixture studied (leading to larger enthalpies and entropies for the formation of this species) than expected on the basis of group additivity calculations. For example, cis, cis-2,4-hexadiene would be expected to comprise 24% of the products at 400 °C on the basis of calculated equilibrium data, whereas the experimentally determined value was about 8.5%. The reasons for this discrepancy are unclear, although under the conditions of temperature and for the time intervals required to drive the high activation energy reactions to equilibrium, evidence of substantial fragmentation was observed. This raises the possibility that populations of the least stable compounds were perturbed so that true equilibrium was never established. Therefore, the predicted equilibrium parameters may be interpreted as representing an upper limit for the fraction of less stable isomers such as cis-1,3-hexadiene or cis, cis-2,4-hexadiene which may occur in a mixture in thermal equilibrium. The thermodynamic parameters attained in this study indicate that the actual amount of such isomers may be less by as much as a factor of 3. Despite this, the relative stability of the hexadiene isomers is clear with trans, trans- and cis, trans-2,4-hexadienes being the most stable and of roughly equal stability, followed by cis, cis-2, 4-hexadiene, then trans- and cis-1, 3-hexadiene.

Thermal Isomerization Mechanism. Two mechanisms with differing energy requirements exist by which *cis,trans*-2,4-hexadiene may rearrange to the other isomers in the conjugated hexadiene system. The low activation energy pathway is the 1,5 sigmatropic rearrangement; a concerted reaction involving hydrogen transfer through a six-membered cyclic transition state.^{32,33}

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(b) Danen, W. C. Opt. Eng. 1980, 19, 21-28. (c) Garcia, D.; Keehn, P. M. J. Am. Chem. Soc. 1978, 100, 6111-3.

⁽³¹⁾ Benson, S. W.; Egger, K. W.; Golden, D. M. J. Am. Chem. Soc. 1965, 87, 468-76.



Figure 6. Schematic of proposed isomerization pathways in the conjugated hexadiene isomer system. Also depicted are the barriers to isomerization and the relative thermodynamic stabilities of the species.

Constraints in geometry imposed by this transition state account for a lower preexponential factor than encountered in other reactions in the system, and, as will be seen, under certain conditions of laser excitation this offsets the advantage of the low reaction threshold. The kinetics of this concerted isomerization has been well studied by Frey for the reaction of cis-1,3-hexadiene to yield cis,trans-2,4-hexadiene.32

Our own investigation of the thermal reaction of trans-1,3hexadiene is interesting in that we find *cis,trans*-2,4-hexadiene as the major product with very little cis-1,3 isomer being formed. This suggests the possibility of a direct concerted reaction between the two species. However, the major 1,3-hexadiene product starting from *cis,trans*-2,4-hexadiene is always *cis*-1,3-hexadiene. This would suggest that isomerization of the trans-1,3 isomer actually procedes via the cis isomer through a high activation energy process which is then followed by an immediate lower activation energy rearrangement of that species to cis, trans-2,4hexadiene. This latter hypothesis seems to be born out by the results of pulsed laser experiments in which irradiation of trans-1,3-hexadiene always produced significant cis isomer in addition to cis, trans-2, 4-hexadiene (Table III and Figure 4). A schematic of the proposed isomerization pathways is shown in Figure 6.

Figure 4 shows the yield of cis-1,3-hexadiene from trans-1,3hexadiene increases relative to the yield of the other dienes as the pressure of argon increases. The behavior is consistent with *cis*-1,3-hexadiene being the primary reaction product and the other hexadiene isomers resulting from further reaction of the primary product. This behavior is also consistent with that of ref 29 where it was shown possible to stop an $A \rightarrow B \rightarrow C$ reaction at step B even though the $B \rightarrow C$ step occurred with high efficiency in a thermally heated system.

All of the above observations can be rationalized by a

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

kinetic pathway where A, B, and C represent trans-1,3-, cis-1,3-, and cis, trans-2,4-hexadienes, respectively. If k_2 is much larger than k_1 then in a thermal experiment, **B** would not build up to any significant steady-state population. In making the steady-state approximation, the ratio of population between B and C is merely given by k_1/k_2 , which over the range of the thermal experiment varies from 2.0 \times 10⁻³ at 470 K to 6.9 \times 10⁻³ at 543 K.^{26,35}

For isomerization in the reverse direction, the activation energy for the reaction of cis, trans-2,4-hexadiene to the cis-1,3 isomer is considerably less than that for the reaction of the cis-1,3 to

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trans-1,3 isomer so that, in a thermal experiment run at moderate temperatures, cis-1,3- could be produced from cis, trans-2,4-hexadiene without production of the trans-1,3 isomer. In the forward direction relatively more of the intermediate isomer B would be expected in the pulsed laser experiments because quenching processes in a nonequilibrium system may intercept B before it has a change to further react to yield C.

The actual situation is not quite this simple since both reactions are reversible. If we take into account the ΔH and ΔS values for the reactions, the back-reaction rates can be calculated for both reactions. The reaction rate from isomer C to B, k_{-2} , is significantly reduced (by approximately an order of magnitude) over k_2 at the temperature at which the thermal reactions were run. Even with the back-reaction rate k_{-1} being similar in magnitude to k_1 , the conclusions drawn above are qualitatively valid since the large value of k_2 relative to the other rate constants in the system prevents the buildup of a significant quantity of species B when the starting material is $A.^{35}$

The high barrier channels in the hexadiene system are those by which *cis,cis*- and *trans,trans*-2,4-hexadienes interconvert with the cis, trans isomer. Both reactions proceed through rotations about a double bond, most likely involving formation of a biradical intermediate.²⁸ The activation energies for cis-trans isomerization are lower than those for unconjugated systems, but considerably higher than that for the sigmatropic rearrangement. However, Arrhenius factors for cis-trans isomerization are larger by several orders of magnitude than for sigmatropic rearrangements due to relaxed constraints upon transition-state geometries.^{28,32,34}

For conjugated dienes, an alternative cis-trans isomerization pathway exists involving formation of a transient cyclobutene intermediate. This pathway was invoked by Frey³⁶ to account for measured rate parameters for the cis to trans isomerization of 2,3-dimethyl-1,3-pentadiene. Neglecting steric factors, one can estimate that, for isomerizations of conjugated dienes, this pathway is preferred by about 10 kcal/mol over alternative (biradical) pathways. Even so, we doubt that it occurs in the cis/trans interconversion of the 2,4-hexadienes. This conclusion is based principally upon observed product yields and the magnitude of measured rate parameters. Specifically, symmetry rules for ring closure and opening²³ dictate that cyclobutene derived from trans, trans-2,4-hexadiene may only form the cis, cis or the original trans, trans isomer. Similarly, the symmetry-allowed products of the cis, cis isomer are either itself or the trans, trans isomer and cis,trans-2,4-hexadiene may produce only itself by means of a cyclobutene intermediate. Since Frey³⁶ has estimated an added energy increment of 5-10 kcal/mol for an "inward" rotation of each methyl group, it is doubtful that the trans-3,4-dimethylcyclobutene formed from either the trans, trans or cis, cis isomer would produce anything but trans, trans-2,4-hexadiene.

Additionally, the s-cis configuration of the cis, cis isomer which is necessary for ring closure would be expected to be highly disfavored sterically. In pyrolysis of cis-3,4-dimethylcyclobutene, the cyclic intermediate expected from *cis,trans*-2,4-hexadiene yielded only about 0.005% of the Woodward-Hoffmann nonallowed trans, trans isomer^{36,38} and, apparently, none of the cis, cis compound. Brauman and Archie have shown the symmetry disallowed transition states to be ≥ 15 kcal/mol above the allowed one, corresponding to the activation energy expected for the biradical intermediate.³⁷ Finally, the magnitudes of the Arrhenius A factors measured in this work for the 2,4-hexadienes are more consistent with a biradical than a concerted mechanism.²⁸ It is difficult to rationalize the experimental product ratios achieved in either thermal or pulsed or CW laser studies with a mechanism which exclusively involves a cyclobutene intermediate. Specifically it would be very difficult to account for the observed formation of significant quantities of cis, trans isomer from either cis, cis- or trans, trans-2, 4-hexadienes as a starting material. Thus if a

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(37) Brauman, J. I.; Archie, W. C., Jr. J. Am. Chem. Soc. 1972, 94, 4262.
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concerted mechanism occurs for the cis, trans isomerization of the 2,4-hexadienes, it is probably a minor component.

The results of CW laser-induced reactions were compatible with the reaction paths discussed above as established by a combination of thermochemical kinetic data and pulsed laser-induced reaction data. The CW laser-driven reactions come about as a result of vibrational deactivation of the nonreactive SF₆ absorber leading to heating of the translational degrees of freedom of the SF₆hexadiene mixture. Since the result of this process is transient heating of the sample which induces a homogeneous gas-phase reaction, it is not surprising that the reaction pathways are consistent with normal thermal reaction processes.

Laser-Induced Isomerization Mechanism. In an earlier publication, we reported on the feasibility of using selective pulsed laser excitation to drive endoenthalpic reactions within the system of conjugated hexadienes and so generate products which did not reflect thermal equilibrium.^{15,16} In addition to the prospect of being able to control the direction of a reaction, we were also interested by the observation of multiple product formation from a single parent species, after only a single laser pulse. Additionally a significant dependence of the isomer product ratios on both fluence and added quenching gas pressure was observed.

Addition of quenching gas to a multiphoton excited system can have a variety of effects on the system. As seen in the work in ref 29, addition of rare gas can be used to quench the second step in an $A \rightarrow B \rightarrow C$ reaction sequences. Thus even a thermal reaction that proceeds to C with high efficiency can be quenched and product B isolated. This was demonstrated in ref 29 for the system trans-1,3,5-hexatriene \rightarrow cis-1,3,5-hexatriene \rightarrow 1,3cyclohexadiene. Similar behavior has been discussed for the isomerization of trans-1,3-hexadiene where addition of rare gas favors the production of cis-1,3-hexadiene. Similar behavior is also observed with trans-2,4-hexadiene as a parent. Addition of rare gas favors production of cis, trans-2,4-hexadiene relative to the other conjugated hexadienes. This further reinforces the hypothesis that isomerization takes place via a series of steps each of which follows the primary isomerization pathways for a system in thermal equilibrium.

Under appropriate circumstances, the change in reaction yield as a function of rare gas pressure can be used to estimate the time scale of reaction and thus the degree of excitation of the parent compound. For example, at 200 mtorr of rare gas, there will be approximately one collision per microsecond. Since this pressure corresponds to the approximate half-quenching pressure for cis, cis-2, 4-hexadiene produced from cis, trans-2, 4-hexadiene, it implies that, assuming strong collisions, isomerization also occurs on approximately the microsecond time scale. In fact, the quenching efficiency should be given by $\omega/(\omega + k_e)$ where ω is the collision rate and k_e the reaction rate.²³ Since the parent hexadiene can also quench the excited parent an extra term, ω' , should be added to the numerator and denominator. This treatment neglects the fact that the reactions observed are reversible and coupled and assumes gas kinetic quenching efficiencies. Nevertheless, this type of treatment should provide an approximate energy for the average reacting molecule. Using the aforementioned treatment, with reference to Figure 1, one finds this energy is ~ 87 kcal/mol.

The effect of fluence on branching ratios for competing reactions is readily seen for the reaction of cis,trans-2,4-hexadiene (see Figure 5) for which two high activation energy, high A factor channels to the trans,trans and cis,cis isomers compete with a low barrier, low preexponential pathway to cis-1,3-hexadiene. Hence, it might be expected that the distribution of products from cis,trans-2,4-hexadiene would reflect changes in the degree of excitation of the parent molecule. Molecules having energies in excess of the lower reaction threshold but below or only slightly in excess of the higher thresholds should rearrange primarily to cis-1,3-hexadiene. This corresponds to the situation in thermally excited systems which at low or moderate temperatures may have significant population capable of reacting through the low barrier channel, but relatively few molecules with energy sufficient to surmount higher barriers.

For laser-excited systems, a different situation may exist. Rapid excitation may produce energy distributions characterized by a high degree of vibrational excitation. In this case, the high activation energy channels may gain prominence or even dominate the system. This is aptly demonstrated in Figure 1, in which the relative magnitudes for certain reaction rates, specifically isomerization of cis.trans-2.4-hexadiene to cis-1.3-hexadiene and cis, cis-2,4-hexadiene, are seen to change with increasing vibrational energy. Above ~ 87 kcal/mol, the high barrier channel to the cis, cis isomer is actually predicted to dominate, due to a preexponential factor \sim 1000 times greater than that for the low barrier reaction to cis-1,3-hexadiene. Thus it is evident that variation in the level of excitation should produce a marked effect on observed branching ratios with an increased disposition toward the high A factor reactions at higher energy. This behavior, as seen in Figure 5, is experimentally observed. The higher barrier channel becomes relatively more important as the fluence is increased.

A second method of estimating the energy of a typical reacting molecule is possible by considering relative yields of the different isomers with cis, trans-2,4-hexadiene as parent. Since all the products result from the same parent, they all come from the same initial energy distribution. Thus the ratio of products contains in it information about the population distribution convoluted with the RRKM rate constants for each channel. If it is assumed that reacting molecules are in the tail of the population distribution, then it is likely that the number of excited molecules decreases rapidly with increasing energy. If this assumption is accepted, then since RRKM rate constants increase rapidly with increasing energy, the convolution of these two functions will result in a small energy region in which a large fraction of reacting molecules are located. With this approximation it should be possible to identify this energy regime via a comparison of RRKM rate constants with branching ratios. Similar assumptions were implicitly made when approximate energies of reacting molecules were calculated from quenching data. When this is done for a fluence of 3.5 J/cm^2 the prediction is that reaction occurs for molecules in an energy range between 70 and 80 kcal/mol, slightly lower than what was predicted from rare gas quenching data. It should be realized that this is an approximate number due to the previously mentioned assumptions and the neglect of back-reactions. It is also dependent on the magnitude of calculated RRKM rate constants which in turn depend on thermal rate data which have finite errors. The differences in the estimates via this and the other method that was previously described are most likely due to these approximations and sources of error.

Clearly variation of fluence will influence branching ratios as the fluence determines the energy of the average reacting molecule. As seen in Figure 5 at 3.5 J/cm², high barrier vs. low barrier products are present in ratios of approximately 1:10. This ratio increases steadily with fluence so that at 6.5 J/cm² the formation of *cis*,*cis*-2,4-hexadiene proceeds at a rate of 1/2 that for formation of *cis*-1,3-hexadiene. If we compare the calculated rates for these reactions, the parent distribution of reacting molecules is estimated to shift by an amount corresponding to an average absorption of six additional photons in going from 3.5 to 6.5 J/cm². This corresponds to the average reacting molecule going from 75 \pm 5 to 90 \pm 5 kcal/mol. Interestingly this number is compatible with calorimetric measurement of absorbed energy. In going from 3.5 to 6 J/cm² the amount of absorbed energy changes by 7 \pm 1 photons/molecule.

Predicted branching ratios clearly depend on calculated RRKM rate constants. Though there is certainly some potential variability it is unlikely that this variability will significantly affect the predicted energy regime. These predictions place the reactant in an energy regime comparable to or slightly exceeding the lowest bond energy in the molecule, e.g., $C-CH_3 \simeq 85$ kcal;³⁹ however, fragmentation does not become a competitive process until somewhat higher energies have been reached. To understand this,

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it is necessary only to compare rates for isomerization to those for loss of a methyl group. This seems to be the preferred fragmentation path since the predominant breakdown product is cyclopentadiene.¹⁵ If we assume a rate constant for fragmentation described by $E_a = 85$ kcal, $A = 10^{16}$,⁴² the classical RRK formula given by

$$k_{\rm J} = A \left(\frac{E_{\rm J}^* - E_{\rm a}}{E_{\rm J}^*} \right)^{S-1}$$

where S is taken to be equal to half of the number of vibrational modes shows the ratio of the fragmentation reaction rate constant to isomerization rate constant is $\sim 10^{-6}$ at 100 kcal, and is ~ 1 at 130 kcal.³² Fragmentation, which does start to occur at >7 J/cm², is likely caused by some beam inhomogenity and/or the very high energy tail of excited molecules. These results also set an upper limit for the degree of excitation in the system.

We are now in a position to consider in more detail the source of secondary products in the system. A number of explanations appear plausible and include the following:

1. Primary products are formed which, due to the almost thermoneutral nature of the isomerization reactions, will often have enough energy to further isomerize, either to another species or back to the parent species. This process which might be called "vibrationally adiabatic" can be disrupted by collisional deactivation. Secondary products formed via this mechanism will be obtained in ratios reflecting the relative volume of phase space occupied by the secondary products convoluted by the energy distribution of the primary product.

2. Primary products may form, absorb additional CO_2 laser photons, and further react. This process would require the initial reaction to occur within the laser pulse so that initial products can form while there is still a source of infrared excitation. Secondary products generated via this process would still be expected to form in ratios characteristic of their relative volumes of phase space convoluted by an energy distribution; but the energy distribution would be expected to be that of the primary product supplemented by absorption of additional photons.

3. Secondary products are formed by reaction processes not accessible to thermal reactions. For example, it could be hypothesized that secondary products are formed in a single-step process. An ergodic single-step process involving two simultaneous double bond isomerizations or a simultaneous sigmatropic rearrangement and double bond isomerization would be expected to have a significantly higher activation energy than biradical isomerization, since it is not observed in thermal systems. As we have shown, fragmentation would be expected to compete more efficiently than it does with such an isomerization process. Another possibility is that a nonergodic process is occurring which allows for the opening up of a specific nonthermal isomerization pathway which takes a parent directly to a secondary thermal product. Primary products would be explained by normal thermal pathways competing with these exotic pathways. Since all of the observations associated with the hexadienes can be explained by RRKM behavior in a transiently excited system (vide infra), there is no evidence to indicate that nonergodic effects are occurring or nonthermal pathways are available to the excited molecules. Though we believe these effects do not occur, as a caveat it should be mentioned that our experiments would not be sensitive to small contributions from nonthermal pathways or processes. Thus we are left with two likely possibilities, 1 and 2.

A variety of evidence already exists which indicates that, as observed in other moderately excited systems,⁴¹ most reaction occurs after the laser pulse. This would imply that mechanism 1 is the operative mechanism for formation of secondary products. If secondary products do indeed come from a "vibrationally adiabatic" process then it should be possible to predict secondary branching ratios if the initial degree of excitation is known. This can be determined via photoacoustic measurements. *trans*,- trans-2,4-Hexadiene was irradiated at 3.0 J/cm² where its product branching ratios were well-known. At this fluence level the magnitude of its photoacoustic signal was measured. cis, trans-2,4-Hexadiene was then placed in the photoacoustic cell and the fluence level was then found that gave the same magnitude photoacoustic signal. Figure 5 was then referred to to determine the branching ratio of cis, trans-2,4-hexadiene at this fluence level. This would be the branching ratio (neglecting the small change energy due to ΔH of reaction) expected for "vibrationally adiabatic" formation of cis, trans-2, 4-hexadiene from trans,trans-2,4-hexadiene where the latter was the parent species and was irradiated at 3.0 J/cm^2 . The predicted ratios for *cis,cis*-2,4-hexadiene and cis- and trans-1,3-hexadiene are 0.24:1.0:0.17 and the observed ratios are 0.23:1.0:0.12. The above treatment assumes that heat capacities for trans, trans-2,4 and cis, trans-2,4 isomers are identical while in fact they differ by 4%, a negligible difference.

Though this agreement in itself does not establish that secondary isomerization occurs via a vibrationally adiabatic process it is supportive, particularly taken in conjunction with other evidence. The reaction half-life of the average molecule at typical reaction energy is in the microsecond range; these molecules will not react until the more intense part of the laser pulse is complete and the tail is virtually over. This result is compatible with a variety of other experiments indicating that most reactions in weakly to moderately excited systems occur after the laser pulse is over⁴¹ and further supports mechanism 1. Absorption of one additional photon would change the expected branching ratio to 0.35:1.0:0.21, outside our experimental error though not prohibitively so. Thus we cannot rule out some sequential absorption competing with or supplementing an isomerization process that yields secondary isomers primarily via a vibrationally adiabatic pathway.

Conclusions

Isomerization reactions in multiple-component isomeric systems may be effected in substantial yields with minimal losses to decomposition through selective infrared multiple-photon excitation of a parent species. The preferential formation of a desired product is possible due to vibrational frequency shifts between isomers, which allows preferential excitation and reaction of specific isomers. Once formed, these products may accumulate over the course of many laser pulses.

At sufficiently high levels of excitation the formation of different products from a single parent species is observed after irradiation with a single laser pulse. The branching ratios of these products reflect the relative magnitude of rates for competing reaction channels whether the products originate directly from the excited parent or, as observed in some instances, through sequential rearrangement of product molecules. Yields and relative abundance of product isomers are fully compatible with reactions proceeding by way of reaction channels which are identical with those followed by thermally excited systems. Thus, it is reasonable to conclude that, at the energy levels necessary for reaction, randomization of energy in excited molecules is complete. A simple model based upon this assumption and using RRKM calculated rate constants is adequate to account for observed branching ratios and, by means of this, predict the degree of excitation attained by the reacting species. It is likely that reactions producing products which cannot occur via single-step thermal pathways occur in a vibrationally adiabatic fashion.

Upon addition of an inert collision partner to the reaction system there is no enhancement of absorption. Rather, the effect observed is a quenching of product formation, even at low rare gas pressures. Whenever product distributions reflect a competition between direct channels of differing activation energies, higher rare gas pressures would be expected to increase the fractional yield of products from reactions having the lowest activation energies. When an $A \rightarrow B \rightarrow C$ process is possible, an increase in quench gas pressure can be expected to increase the relative yield of B versus C even if the $B \rightarrow C$ rate constant is larger than the $A \rightarrow$ B rate constant. In a related manner, increasing the laser fluence has the effect of increasing the fractional yield of high activation

⁽⁴⁰⁾ Assuming homogeneous bond fission. See ref 15.

⁽⁴¹⁾ Quack, M.; Humbert, P.; van der Bergh, H. J. Chem. Phys. 1980, 73, 247.

energy products due to the more rapid increase in magnitude of the rates of high activation energy reactions with energy.

Thus, by controlling the energy input in a multiple-component system, the composition of the system may be profoundly effected, and conditions may be selected in which the yield of a desired component is enhanced. The degree of stimulation of the system may be regulated by variation of laser intensity, and both the level of excitation and reaction time may be collisionally controlled. With the appropriate selection of the excitation wavelengths as a further option, the control of reaction systems using infrared lasers may be realized. Though this control is certainly not mode-selective chemistry, it is selective laser chemistry.

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Registry No. trans, trans-2,4-Hexadiene, 5194-51-4; cis, cis-2,4-hexadiene, 6108-61-8; trans-1,3-hexadiene, 20237-34-7; cis-1,3-hexadiene, 14596-92-0; cis,trans-2,4-hexadiene, 5194-50-3.

Picosecond Time-Resolved Fluorescence Spectroscopy of Molecular Vapors

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The first results on the time gating of the UV fluorescence spectra of molecular vapors by frequency downconversion with multichannel detection are presented. A downconversion gate with a temporal width of 10 ps and a useful spectral width of ca. 1200 cm⁻¹ has been developed. Preliminary data on the collision free fluorescence spectra of p-difluorobenzene vapor have been obtained for the 3¹30³ level at time delays after excitation of 3, 10, and 27 ps. Collisional redistribution, evidenced by spectral broadening, was observed and estimated to occur with a cross section exceeding hard sphere.

Introduction

In recent years there has been much interest in the process of intramolecular rovibrational energy redistribution in isolated molecules.¹⁻¹⁵ Experiments have been devised to test the effects of vibrational energy content,^{5,6} vibrational state density,⁷⁻⁹ and mode selectivity¹⁰ on redistribution rates. Some of the redistribution rates which have been inferred from these experiments are on the picosecond time scale. Recently this laboratory reported on the direct measurement of intramolecular relaxation in the S_1 electronic manifold of p-difluorobenzene under collisionless conditions.¹⁶ The experimental method was picosecond-time-resolved fluorescence spectroscopy by frequency downconversion.

Fluorescence spectroscopy can be used to probe the rovibrational dynamics of electronically excited polyatomic molecules because the spectra are excitation specific. Examples of the use of fluorescence spectroscopy as a probe of vibronic level population dynamics include the determination of propensity rules for vibrational energy relaxation from a single vibronic level due to collisions¹⁷⁻²⁰ and to vibrational predissociation of van der Waals complexes.²¹ Relative cross sections of the various level-to-level relaxation pathways are measured in these steady-state experiments.

New technology has now made possible the acquisition of picosecond-time-resolved fluorescence spectra of molecular vapors. The first results with multichannel detection are presented herein. In particular, time-gated spectra of p-difluorobenzene vapor under collisionless and collisional conditions have been obtained. A detailed discussion of the experimental requirements is presented.

Methods

The experimental constraints for time gating the fluorescence of molecular vapors by frequency downconversion are rather severe. A picosecond laser system which can provide both tunable pulses for state specific excitation and high peak power optical frequency gating pulses for efficient, noise-free gating is required. The detection system should enable a large spectral region of the gated fluorescence from a single laser shot to be displayed.

⁺N.S.F. Predoctoral Fellow.

A schematic of the downconversion gate developed for this work is shown in Figure 1. An important feature of this design is that the collection lens L1 focuses the fluorescence into the gating crystal with a wide distribution of input angles which allows a broad band of frequencies to satisfy the phase-matching conditions. For a given angle ϕ between the gating laser and fluorescence wavevectors, the wavevector mismatch is

$$\Delta k = k_{\rm s} - [k_{\rm f}^2 + k_{\rm l}^2 - 2k_{\rm f}k_{\rm l}\cos\phi]^{1/2} \tag{1}$$

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