A RAND NOTE

LASER-INDUCED DESTRUCTION OF HAZARDOUS CHEMICALS: A PRELIMINARY ANALYSIS

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PREFACE

The increasing reliance on various chemicals in all facets of society has led to a very high level of annual atmospheric emissions. Many of the emitted chemicals are dangerous; some may deplete the protective ozone layer, others contribute to photochemical smog, some are carcinogenic or mutagenic.

Methods for minimizing the emissions of hazardous chemicals are actively being sought by U.S. government agencies, especially the Environmental Protection Agency. This study, supported by The Rand Corporation from its own funds, is an initial analysis of a novel technique for decomposing certain dangerous chemical gases before they are released to the atmosphere.

Decomposition of these gases would be accomplished with a carbon dioxide laser. Photodissociation in specific cases would generate products that are less dangerous than the original chemical. The method appears promising as a means of reducing the deleterious effects of certain widely used industrial chemicals.

SUMMARY

Society's increasing dependence on chemicals in recent years had led to the production of vast amounts of solid, liquid, and gaseous wastes. The Resource Conservation and Recovery Act (RCRA) was designed to control solid and liquid hazardous waste products once they were generated. The Clean Air Act and other state regulations were promulgated to minimize the emission of dangerous gases. The Environmental Protection Agency (EPA) and other government agencies have expressed an interest in technical methods that might prove effective in destroying dangerous chemicals before they leave the plant environment and become subject to regulation. This study evaluates one such technique, laser infrared multiphoton dissociation, for decomposing deleterious chemical gases.

One especially dangerous class of chemical is the one consisting of the chlorinated hydrocarbons. Members of this species can cause photochemical smog or may contribute to ozone completion; some members are extremely carcinogenic and mutagenic and pose serious consequences to workers and society as a whole. In this Note, we focus on the destruction of two hazardous series of these chemicals, the chlorinated ethylenes and the chlorinated ethanes. We present a detailed method for decomposing chlorinated chemicals in the workplace using a relatively inexpensive CO_2 laser.

Our initial results show that CO_2 laser photodegration of vinyl chloride, a chlorinated ethylene, is promising. This chemical is highly carcinogenic and mutagenic; it is used primarily as a precursor chemical

in the production of polyvinyl chloride. In the photodissociation of vinyl chloride, acetylene (C_2H_2) and hydrochloric acid (HCl) are produced. Acetylene poses an insignificant threat and HCl neutralization can be accomplished straightforwardly. Although vinyl chloride serves as the main example throughout, we also focus on the destruction of other dangerous chemicals including vinylidene chloride, trichloroethylene, ethylene dichloride, and 1,1,1-trichloroethane. This research was performed as background for a proposal recently sent to EPA. The preliminary analysis presented here shows that laser dissociation of chlorinated chemicals holds promise. However, further work, including an experimental investigation, is necessary to establish the technical feasibility of the method.

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I. INTRODUCTION

Over the last two decades, society has become increasingly dependent on a number of different substances that are extremely useful for various industrial purposes. As a result, a great amount of solid, liquid, and gaseous waste is being created. Recently, photodegradation techniques for decomposing dangerous chemicals have become of interest. Depending on the particular technique, it may dissociate species in the gas, liquid, or solid phase. In this Note, we examine one method--laser infrared multiphoton dissociation--which can be applied to chemicals in the gas phase.

It is now well established that emission of certain substances widely used in industry may have deleterious consequences. In the last decade, research has shown that many of these chemicals are extremely toxic, and some are carcinogenic, mutagenic, and teratogenic. Some species decompose in the troposphere and contribute to the formation of photochemical smog; others remain intact until they reach the stratosphere, where they are suspected of depleting the ozone layer. Because of the danger to workers from short-term toxic effects, regulations require that most noxious chemicals be diluted with air before they are emitted from the workplace. Regulations also sometimes limit the absolute amount of emissions from each emitting source because of concern for long-term toxic effects. In spite of these efforts, and because of the growing number of sources and society's increasing reliance on chemicals, current annual emissions of hazardous chemicals are enormous in the aggregate.

Government agencies, especially the Environmental Protection Agency (EPA), are presently examining methods for decomposing dangerous chemicals before they are emitted to the atmosphere. In this Note, we present an initial evaluation of the potential of a novel technique for destroying chlorine-containing chemicals. The technique uses a laser to institute photodecomposition. Most of the research on laser multiphoton dissociation is basic and does not consider applications. Our analysis uses the results of the available theoretical and experimental work in this area to assess the technical feasibility of developing a practical method for destruction of dangerous chemicals before they are emitted.

Dissociation of hazardous chlorinated chemicals would be accomplished with a carbon dioxide (CO_2) laser either in a production plant or an industrial setting. The academic literature indicates that laser irradiation of several chlorinated species will break the chlorine bond. This suggests that the method would be useful for photodegradation. Indeed, our initial investigations confirm that laser multiphoton dissociation offers promise for preventing the emission of some extremely hazardous gases.

In Sec. II, we present environmental, toxicity, and production information for four analog series of chlorine-containing chemicals. We then review the available experimental data for each of these chemicals.

In Sec. III, we provide the rationale for focusing the study on certain classes of chemicals. In addition, we present a brief description of the industrial conditions under which emissions of these chemicals occur. We also discuss the particular advantages offered by using the laser to effect decomposition.

In Sec. IV, we describe the specific aims that should be accomplished in future work and in Sec. V we outline the methods that could be used to accomplish them. In general, the aims include adapting the theoretical models and using the existing experimental results to evaluate the technical feasibility of decomposing three especially hazardous chemicals, which form an analog series. We perform a sample calculation, resulting in a preliminary set of laser requirements for decomposition. We next describe an experimental investigation that could be performed on two of the chemicals. The experiments are designed to determine the ability of the theoretical models to predict dissociation yields for analog series of chemicals. We then summarize a plan to theoretically assess the feasibility of the laser technique for decomposing two additional chemicals that are members of a second analog series.

In Sec. VI, we discuss an area of focus for future work.

In Sec. VII, we conclude with a brief summary of the further work needed for assessing the feasibility of the proposed technique.

II. BACKGROUND

In this section, we present certain data for four families of chemicals and discuss the existing experimental results on infrared multiphoton dissociation of each chemical. The information presented here is intended to illustrate that the data base on laboratory decomposition is extensive. In the next section, we discuss the basis for selecting certain chemicals for comprehensive study.

CHEMICALS

Table 2.1 provides a list of four analog series of chlorine-containing chemicals. The list is not intended to be exhaustive and presents only those chemicals for which there is a reasonable industrial demand. For each chemical, we show the 1979 production figures, the primary use, the atmospheric threat, the Threshold Limit Value (TLV),[1] and the potential long-term hazard. These data were compiled from several sources, including ACGIH (1981), U.S. International Trade Commission (1979), Palmer et al. (1980), and Henschler (1977).

The first family of chemicals given in Table 2.1 is the chlorofluorocarbons (CFCs). CFCs are very unreactive; they are thought to reach the stratosphere intact. Within the stratosphere, impinging ultraviolet radiation causes them to decompose. The chlorine produced in the dissociation process reacts with ozone, perhaps leading to

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[1] TLV is the maximum allowable time-weighted average concentration to which a human may be exposed over an 8 hour working day, 40 hour work week. Generally, the more toxic the chemical, the lower the TLV.

Table 2.1

PRODUCTION, USE, AND THREAT OF CHLORINATED CHEMICALS

Common Name	Chemical Formula	1979 Production (millions of pounds)	Primary Uses	Atmospheric Threat	TLV(ppm)	Long-Term Threat
CFC						
CFC-11	$CFCL_3$	167	Flexible and rigid foams	ozone	1000	--
CFC-12	CF_2Cl_2	294	Refrigerant	ozone	1000	--
CFC-13	CF_3Cl	--[a]	Low temperature refrigerant	ozone	1000	--
CFC-22	CHF_2Cl	211	Refrigerant, intermediate	ozone	1000	M
CFC-113	$CFCl_2CF_2Cl$	130	Solvent	ozone	1000	--
CFC-114	CF_2ClCF_2Cl	--[a]	Intermediate	ozone	1000	--
CFC-115	CF_2ClCF_3	--[a]	Refrigerant	ozone	1000	--
CHLOROMETHANE						
methyl chloride	CH_3Cl	463	Silicone and tetramethyl lead manufacture	--	50	--
methylene chloride	CH_2Cl	633	Paint remover, solvent	--	100	M
chloroform	$CHCl_3$	356	CFC manufacture	--	10	R
carbon tetrachloride	CCl_4	714	CFC manufacture	--	5	R
CHLOROETHANE						
ethyl chloride	C_2H_5Cl	582	Tetraethyl lead manufacture	--	1000	--
ethylene dichloride	CH_2ClCH_2Cl	11,794	Vinyl chloride manufacture solvent	--	10	R
methyl chloroform	CH_3CCl_3	716	Solvent	ozone	350	--
CHLOROETHYLENE						
vinyl chloride	CH_2CHCl	6,389	Polyvinyl chloride manufacture	PS	5	R
vinylidene chloride	CH_2CCl_2	--[b]	Polymer manufacture	PS	10	R[c]
1,2-dichloroethylene	CHClCHCl	--[b]	Solvent	PS	200	--
trichloroethylene	$CHClCCl_2$	319	Solvent	PS	100	R
perchloroethylene	CCl_2CCl_2	773	Solvent	ozone	100	R

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[a] Less than 20 million pounds.

[b] Production figures not available from published sources.

[c] Carcinogenic to mice; not all strains of rats.

DEFINITIONS: PS = photochemical smog; M = mutagenic; and R = carcinogenic/mutagenic.

depletion of the ozone layer. The CFCs pose no problems other than their potential for ozone depletion; indeed, as the figures of Table 2.1 show, their TLVs are the highest value assigned, and only CFC-22 has the potential for long-term toxicity.

The chloromethanes, chlorocarbons containing only one carbon atom, have low TLVs, indicating that they present a danger to workers. For this reason, carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) are rarely used as solvents today. In addition to the acute problems, these chloromethanes also pose long-term health threats, so that their emission into the atmosphere is undesirable.

The chloroethanes, chlorocarbons with two carbon atoms and no double bonds, is the third group of chlorinated chemicals that is of interest. The TLV of ethyl chloride, like that of the CFCs, is the highest value assigned; it also poses no long-term health threat. Ethylene dichloride, in contrast, has a low TLV and can pose a threat to health. Methyl chloroform, a widely used solvent, has a fairly low TLV and does not present much of a long-term health threat.

The final family of chemicals we consider is the chloroethylenes, chlorocarbons with two carbon atoms and one double bond. This series includes vinyl chloride, vinylidene chloride, 1,2-dichloroethylene, trichloroethylene, and perchloroethylene. All these have very low TLVs, and three--VC, VDC, and TCE--are carcinogenic and mutagenic.

EXPERIMENTAL DATA

In this subsection, we summarize the available experimental data for the four analog series of chemicals. We are brief in the description of the data on the CFCs and chloromethanes but treat the chloroethanes and chloroethylenes in more detail.

CFCs

The infrared multiphoton dissociation of CFC-11 has been studied in a number of laboratories. In one study (Hudgens, 1978), CO_2 laser irradiation of CFC-11 produced the radicals $CFCl_2$ and Cl. Another group (Sudbo et al., 1979), in a molecular beam experiment, obtained the same products at low laser fluences; at higher fluences, secondary dissociation into CFCl and Cl was observed. Evidence for secondary dissociation at very high intensities of a focused irradiation geometry with a CO_2 laser is also provided by a second group (Morrison et al., 1981).

CFC-12 has been widely studied. One group (Folcher and Braun, 1978) observed that, upon irradiation with a CO_2 laser, CFC-12 dissociated into CF_2Cl and Cl as well as CF_2 and Cl_2, where the atomic elimination accounts for at least 85 percent of the product. In another study (Hudgens, 1978), the same products were obtained in the ratio of 33 parts of CF_2Cl to 1 part of CF_2. Two other studies (Morrison and Grant, 1979; and Morrison et al., 1981) also confirm the formation of the two products.

CFC-13 has been studied by two groups (Dever and Grunwald, 1976; Horwitz et al., 1981). In both experiments, the primary dissociation products were CF_3 and Cl. Secondary dissociation gives CF_2 and F. Radical recombination generates C_2F_6, C_2F_4, and CF_2Cl_2 as final products.

The decomposition of CFC-22 by irradiation with a CO_2 laser has been the subject of several studies (Duperrex and van den Bergh, 1979; Stephenson et al., 1979; Gozel and van den Bergh, 1981). Each of the three studies confirms the production of CF_2 and HCl in the primary dissociation.

The products observed in the initial dissociation of CFC-114 are primarily C_2F_4 and Cl_2 (Grieco et al., 1976). Dissociation of CFC-115 in a crossed laser molecular beam experiment (Krajnovich et al., 1978) leads to the formation of C_2F_5 and Cl at low laser fluences; at higher fluences, CF_3 and CF_2Cl are produced.

In general, the fully halogenated CFCs with one carbon atom (CFC-11, CFC-12, CFC-13) decompose through atomic chlorine elimination upon irradiation with a CO_2 laser. Only very small amounts of products formed through molecular elimination (either as primary or secondary dissociation) are observed. The laser method, therefore, does not appear particularly promising for dissociating CFC-11 and CFC-12 because the radicals formed in the atomic elimination would still contain at least one chlorine atom. The method might be used to decompose CFC-13, since it contains only one chlorine atom to begin with. The industrial use of CFC-13, however, is so infrequent that decomposition would not be worthwhile.

Dissociation of CFC-22, a non-fully halogenated CFC with one carbon atom, yields HCl and CF_2. The CF_2 radical probably dimerizes to C_2F_4, a chemical that appears to pose no toxic or atmospheric threat. Ozone depletion by CFCs has not been established unequivocally. EPA, nevertheless, has assigned each CFC an ozone depletion factor in case the theory is proven to be correct. The ozone depletion factor assigned to CFC-22 is 0.05 (relative to CFC-11 with an assigned factor of 1.00). Hence, even if CFC ozone depletion is proven, CFC-22 is not an especially worthwhile candidate for laser decomposition because its potential threat to the ozone layer is so small.

The fully halogenated CFCs containing two carbon atoms include CFC-113, CFC-114, and CFC-115. The decomposition of CFC-113, a widely used solvent, might be desirable; unfortunately, there are no experimental data on laser decomposition of the chemical. CFC-114, used primarily as an intermediate for manufacturing CFC-115, yields C_2F_4 and Cl_2 upon irradiation (Grieco et al., 1976). CFC-115 is used as one component of the azeotrope CFC-502, a low temperature refrigerant. At low laser fluences, atomic elimination occurs giving C_2F_5 and Cl (Krajnovitch et al., 1978). The radical C_2F_5 probably dimerizes to form C_4F_{10}. There are no data indicating that either C_4F_{10} or C_2F_4, the products from CFC-114 dissociation, would pose a threat. Neither CFC-114 and CFC-115 are particularly good candidates for the laser process, since their production levels (~10 million pounds annually for each) are not significant.

The proposed laser destruction process does not appear especially promising for the CFCs. Those CFCs that yield the most tractable products are CFC-13, CFC-22, CFC-114, and CFC-115. CFC-22 has a very low assigned ozone depletion factor and CFC-13, CFC-114, and CFC-115 are characterized by low annual production rates. One would most like to destroy CFC-113 because its assigned ozone depletion factor is high (0.77) and 1979 production amounted to about 130 million pounds. However, because of the lack of experimental data on this chemical, an evaluation of the feasibility of its destruction is not possible.

Chloromethanes

The infrared multiphoton dissociation of the chlorinated methanes has not been studied widely. One study (Earl and Ronn, 1976) examined the reaction of chlorine with a number of methyl halides, rather than directly focusing on dissociation. A second group (Ambartzumian et al., 1978) studied the efficacy of using the ammonia laser for isotope selection in CCl_4. Another group (Haak and Stuhl, 1979) investigated photolysis of the chloromethanes, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 with an argon fluoride laser that operates in the vacuum ultraviolet region. Decomposition of the latter three species led to the production of Cl_2, probably in an excited electronic state. Decomposition of CH_3Cl yielded CH fragments that were apparently also in an excited electronic state.

The most dangerous of the chloromethanes are CCl_4 (carbon tetrachloride) and $CHCl_3$ (chloroform). Any photodissociation technique (infrared or ultraviolet) resulting in molecular chlorine (Cl_2) elimination would not fully eliminate the chlorine from the fragments formed in the dissociation of CCl_4 or $CHCl_3$. For destruction of these two chemicals, therefore, photodissociation does not appear especially promising. Ultraviolet photodissociation might be appropriate for CH_3Cl (chloromethane) and CH_2Cl_2 (methylene chloride). CH_3Cl is not a particularly good candidate for destruction, however, because its annual production level is very low. CH_2Cl_2 is widely used industrially, both as a solvent and in the manufacture of flexible urethane foam. In flexible foam plants, the methylene chloride is present in dilute concentration in air (Mooz et al., 1981) and the gas stream can be treated in the manner described earlier for solvents. Future work on the destruction of this chemical might be appropriate.

Chloroethanes

Ethyl chloride, the first member of the chlorinated ethane series, has been studied in three laboratories. One group (Bailey et al., 1974) used a CO_2 laser to effect decomposition. A number of products, including C_2H_4, HCl, CH_4, C_2H_2, H_2, and C_6H_6, were detected. Another group, also using a CO_2 laser (Nagai and Katayama, 1978), reported C_2H_4, C_2H_2, and HCl as the dissociation products. A third group (Hai-Lung Dai et al., 1979) used a neodymium laser to effect decomposition; the observed products were C_2H_4 and HCl.

Only one study (Nagai and Katayama, 1978) reported on an investigation of ethylene dichloride, the second member of the chloroethanes. The molecule, at a pressure of 20 torr,[2] was irradiated using the P branch of the 10.6 µm band of the CO_2 laser. The observed products were C_2H_3Cl (vinyl chloride) and HCl. Secondary dissociation was not reported.

Three investigations of the third member of the analog series, methyl chloroform, have been performed. In one study (Preiswerk et al., 1979), the reported products are CH_2CCl_2 (vinylidene chloride) and HCl, which result from a four-center elimination. The experiments were performed by irradiating methyl chloroform in a 10 cm long brass cell with a focused beam of a CO_2-TEA laser. The molecule has an absorption band coincident with the R branch of the 9.6 µm band of the CO_2 laser. To investigate the effect of collisions on the dissociation yield, mixtures of 4 torr methyl chloroform and the buffer gases argon, hydrogen, and oxygen were irradiated in the range of zero to 50 torr

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[2] A torr is a unit of pressure equal to 1/760 of an atmosphere.

buffer gas. The effect of collisions is such that the maximum decomposition was obtained at a yield of about 5 torr partial pressure of buffer gas.

A second group (Nagai and Katayama, 1978) irradiated 20 torr of methyl chloroform at the P branch of the 10.6 µm band of the CO_2 laser. The reported products were CH_2CCl_2 (vinylidene chloride) and HCl.

A different experimental approach was used by the third group to study methyl chloroform (Sudbo et al., 1978b). A supersonic nozzle beam of the molecules was crossed at 90° with the focused beam from a CO_2-TEA laser in a vacuum chamber. The advantage of this technique over laser irradiation of a gas cell is that the experiment will be collisionless and free from wall effects. The products obtained from the crossed beam dissociation of methyl chloroform at 1073.3 cm^{-1} were found to be HCl and CH_2CCl_2 (vinylidene chloride). The resulting CH_2CCl_2 was vibrationally excited, and secondary dissociation was observed. The probable secondary products were identified as C_2HCl (chloroacetylene) and HCl. Although the ground state absorption frequency of vinylidene chloride (1095 cm^{-1}) does not coincide with the experimental irradiation frequency (1073.3 cm^{-1}), the energy provided by the CO_2 laser field is apparently sufficient to cause secondary dissociation of the vibrationally hot vinylidene chloride molecules.

The dissociation of methyl chloroform is an example of a two-step dissociation process. The first step yields vinylidene chloride; the second yields chloroacetylene. Although there are no infrared multiphoton dissociation experimental data for the second step in the dissociation of ethylene dichloride, we suspect that it exhibits an analogous behavior. The first step of the dissociation yields vinyl chloride, whereas secondary dissociation is likely to give acetylene.

Chloroethylenes

Vinyl chloride, the first member of the chlorinated ethylene family, has been studied in a number of laboratories. In all of the studies (Lussier and Steinfeld, 1977; Nagai and Katayama, 1978; Lussier et al., 1978; Reiser et al., 1979; Gandini et al., 1979), the observed products were acetylene (C_2H_2) and HCl.

One group (Lussier and Steinfeld, 1977) irradiated vinyl chloride at several vibrational frequencies in the 9.6 μm and 10.6 μm regions of the spectrum (1046.9 cm^{-1}, 944.2 cm^{-1}, 942.4 cm^{-1}, 932.9 cm^{-1}). In each case, the same products were obtained. In later work (Lussier et al., 1978), the same group investigated the effects of pressure on the yield of the dissociation products. The percentage of vinyl chloride dissociated increases with increasing vinyl chloride pressure over the range 0.5 to 20 torr. When helium is added to the vinyl chloride as a buffer gas in the range zero to 40 torr, the fraction of vinyl chloride dissociated declines. In later work (Reiser et al., 1979), this group verified that the mechanism of HCl elimination is α, α elimination; that is, the H and Cl atoms are eliminated from the same carbon atom.

Another group (Nagai and Katayama, 1978) irradiated pure vinyl chloride with a CO_2 laser at pressures between 10 and 50 torr. The primary products were C_2H_2 (acetylene) and HCl. In another study (Gandini et al., 1979), vinyl chloride was irradiated with a CO_2 laser at various pressures between zero and 2.5 torr. This group reported obtaining C_2H_2 (acetylene) and also a small amount of C_2H_4 (ethylene). The relative yield of C_2H_4 is enhanced at pressures below about 0.5 torr.

It should be noted here that vinyl chloride decomposition is probably the second-step product in the dissociation of ethylene dichloride, the second member of the chloroethane series. Similar to that observed in the decomposition of methyl chloroform (Sudbo et al., 1978b), this vinyl chloride product is likely to be vibrationally excited. Hence, very little additional energy may be required to dissociate the excited vinylidene chloride molecules making the process somewhat different from decomposing vinylidene chloride initially in the ground vibrational state.

Two of the same groups investigating vinyl chloride have also studied vinylidene chloride. In one study (Nagai and Katayama, 1978), irradiation of up to 10 torr vinylidene chloride at the R branch 9.6 μm band of the CO_2 laser produced the products C_2H_2 (acetylene) and C_2HCl (chloroacetylene) in the ratio of one to five. In a second study (Reiser et al., 1979), decomposition at about 10 torr of vinylidene chloride yielded the products C_2HCl (chloroacetylene) and HCl. It should be noted here that vinylidene chloride (CH_2CCl_2) is one of the elimination products in the first step of the dissociation of 1,1,1-trichloroethane, the third member of the chloroethane group.

Irradiation of trans-dichloroethylene (CHClCHCl) yields interesting results, and this molecule has been studied by a number of researchers (Nagai and Katayama, 1978; Reiser et al., 1979; Katayama and Mizugai, 1979). The primary product is cis-dichloroethylene; only small amounts of the elimination products chloroacetylene (C_2HCl) and HCl are observed. The primary product, cis-dichloroethylene, does not absorb CO_2 radiation, so that decomposition of the cis isomer does not occur.

The dissociation of trichloroethylene using a CO_2 laser has been studied widely (Sudbo et al., 1978a; Nagai and Katayama, 1978; Reiser et al., 1979; Katayama and Mizugai, 1979). Upon irradiation of 18 torr of trichloroethylene at the 10.6 μm band of the CO_2 laser, Nagai and Katayama (1978) reported the production of C_2Cl_2 (dichloroacetylene) and C_2HCl (chloroacetylene) in a ten to one ratio. In a second study (Reiser et al., 1979), the primary product of irradiation of 10 torr of trichloroethylene was C_2Cl_2 (dichloroacetylene); a small amount of C_2HCl (chloroacetylene) was also observed. A third group (Sudbo et al., 1978a), using the crossed molecular beam technique, obtained the radicals C_2HCl_2 and Cl. Apparently, this method, which avoids wall effects and collisions, leads to Cl elimination rather than HCl elimination.

Vinyl chloride, vinylidene chloride, trans-dichloroethylene, and trichloroethylene have also been studied with a vacuum ultraviolet laser. Products obtained from irradiation of vinyl chloride and vinylidene chloride are acetylene (C_2H_2) and chloroacetylene (C_2HCl), respectively, the same as obtained in the CO_2 infrared laser experiments. The ultraviolet dissociation of trichloroethylene leads to chloroacetylene (C_2HCl) and Cl; this result differs from the reported infrared decomposition products obtained using both direct irradiation and the molecular beam technique. The infrared irradiation of trans-dichloroethylene yielded primarily the cis isomer, whereas ultraviolet irradiation caused decomposition to chloroacetylene (C_2HCl) and HCl.

We have been unable to identify any studies of perchloroethylene, the fourth member of the chloroethylene series.

LASER CHEMISTRY AND PRODUCT TOXICITIES

We mentioned in the Background section that the most commonly used chlorocarbons have either significant toxicities or environmental threats associated with them. The principal motivation for investigating laser destruction of these compounds is to remove these threats but this requires that the reaction products be known and not pose serious problems themselves.

The infrared multiphoton products of the chloroethylenes and some chloroethanes are already known at values of the fluences sufficient to access the lowest energy decomposition channel. These are summarized in Table 2.2.

The first five compounds make up the complete chloroethylene series except perchloroethylene. The laser products of this compound in its pure state are not known but are qualitatively quite different from the others, since the absence of a hydrogen atom makes dehydrohalogenation impossible. Trans-dichloroethene will absorb radiation at the P(30), 10.6 μm line isomerizing to cis-dichloroethane; the cis form, however, will not absorb radiation at this frequency (unless the intensity is greatly increased above that used by Reiser et al., 1979) and thus the cis form becomes the primary product.

Of the chloroethanes, the decomposition products of trichloroethane and ethylene dichloride are known. The laser data of Nagai and Katayama (1978), as well as thermal data (Benson and O'Neill, 1970), show that ethylene dichloride decomposes first into HCl and vinyl chloride (for example, under the action of a CO_2 laser tuned to the 944.2 cm^{-1} P(20) line and matched to the 940 cm^{-1} fundamental of ethylene dichloride (Wu,

Table 2.2

PRODUCTS OF IR LASER DECOMPOSITION

	Reactant	Products	References
1.	Vinyl chloride (CH_2CHCl)	HCl, acetylene (C_2H_2)	Lussier and Steinfeld (1977); Lussier et al. (1978); Nagai and Katayama (1978); Gandini et al. (1979)
2.	Vinylidene chloride (CH_2CCl_2)	HCl, chloroacetylene (ClC_2H)	Reiser et al. (1979); Nagai and Katayama (1978)
3.	Trans-dichloroethene (ClHCCHCl)	Cis-dichloroethene	Reiser et al. (1979); Katayama and Mizugai (1979); Nagai and Katayama (1978)
4.	Cis-dichloroethene (HClCCHCl)	(Unreactive at low fluence)	Reiser et al. (1979); Katayama and Mizugai (1979)
5.	Trichloroethylene (Cl_2CCHCl)	HCl, dichloroacetylene	Reiser et al. (1979); Katayama and Mizugai (1979); Nagai and Katayama (1978)
6.	Trichloroethane (Cl_3CCH_3)	HCl, vinylidene chloride chloroacetylene	Sudbo et al. (1978a, 1978b); Preiswerk et al. (1979); Nagai and Katayama (1978)
7.	Ethylene dichloride (CH_2ClCH_2Cl)	HCl, vinyl chloride acetylene	Nagai and Katayama (1978)

1946). At sufficiently high fluence, vinyl chloride should then go on to yield HCl and acetylene because the vinyl chloride product is so highly excited that additional laser absorption would be nearly independent of frequency, and because the twisting and wagging frequencies of vinyl chloride (941 cm^{-1} and 896 cm^{-1}) (Lussier and

Steinfeld, 1977) are well matched to the CO_2 laser line. Still other chloroethanes (C_2H_5Cl, $CHCl_2CH_3$, $CHCl_2CH_2Cl$) have been photo-decomposed by a CO_2 laser, but these have been excluded from the table because of their relatively low use.

The products in Table 2.2 contain several unstable or toxic species, notably the chloroacetylenes and hydrogen chloride. Acetylene, however, is essentially non-toxic except for its ability to impede an individual's access to oxygen. According to an EPA report by Dimitriades and Joshi (1977), acetylene is also characterized by a poor ability to contribute to the formation of tropospheric ozone, due to its short kinetic oxidation chain. Thus, as a photochemical smog contributor, it is only slightly more reactive than propane (the saturated hydrocarbons are generally ranked at the bottom of the list of photochemical threats) and is far less reactive than ethylene (which is generally ranked at the top).

The risks VC, VDC, TCE, ED, and MC pose as carcinogens or mutagens, smog contributors, or ozone depleters are summarized briefly in Table 2.1. Quantitative measures of the relative risks posed by each compound under consideration are provided by:

- abbreviated dose-response and mutation rate data (such as found in Maltoni (1975), for vinyl chloride, Henschler (1977) for the chloroethylenes, Weisburger (1977) for the halogenated hydrocarbons, and TSCA Interagency Testing Committee (1978);
- threshold limit values (ACGIH, 1980);
- lower atmosphere ozone formation rates (Dimitriades and Joshi, 1977);

- stratospheric ozone depletion factors (Fed. Reg., 1980); and
- present emission standards.

In fact, the investigations of Henschler (1977) have already been useful to us in demonstrating that the asymmetric chloroethylenes (TCE, VC, VDC), the ones most easily decomposed by the IR laser, exhibit more unstable epoxide metabolites and significantly greater mutagenic responses than the other members of the analog series.

III. RATIONALE

In this section, we identify those chemicals that will be treated in more detail, present the rationale for the major theoretical and experimental investigations for a complete analysis, and discuss the two industrial situations in which atmospheric emissions might be prevented. We then describe the advantages of the infrared CO_2 laser for destroying hazardous chemicals.

CHEMICALS FOR DETAILED STUDY

The chemicals that we have selected for study were chosen on the basis of several factors: first, because evidence showed that they could be decomposed by infrared lasers; second, because their production level is high or their decomposition is significant for compounds that are produced in high volume; and, third, because they pose a significant chronic toxicity or atmospheric threat.

Trans-dichloroethylene is produced in relatively low volume and does not decompose to a compound that has a reduced chlorine content (as mentioned in Sec. II, Background) and is, therefore, not considered for detailed investigation. Perchloroethylene is also not considered because no experimental data on its decomposition are available, and its decomposition products are likely to be fully chlorinated.

Vinyl chloride (VC), vinylidene chloride (VDC), and trichlorethylene (TCE), on the other hand, are all decomposed by CO_2 lasers, eliminating hydrogen chloride. VC and VDC are both extremely toxic (see Table 2.1). VC is produced in large volume and VDC, although only produced in small volume itself, is the laser decomposition intermediate of methyl chloroform, which is produced in large volume. TCE is relatively toxic, is a recognized contributor to photochemical smog, and is produced in large quantity. For these reasons we will confine our attention among the chloroethylenes to VC, VDC, and TCE.

Among the chloroethanes we will confine our attention to ethylene dichloride (ED), and methyl chloroform (MC). Both are known to be decomposed by infrared laser radiation, both have high production levels, ED is extremely toxic, and MC is both mildly toxic and a potential threat to the ozone layer.

VC and ED both decompose to relatively innocuous acetylene and (treatable) hydrogen chloride. Hence, there is particularly strong reason to theoretically characterize their photodissociation kinetics and the pressure and laser field requirements for their decomposition. Existing theoretical models can be readily adapted to describe VC decomposition. The characterization of the decomposition of ED requires a more detailed investigation, however, because the reaction is a two-step process with the second reaction being the photodissociation of VC from an excited vibrational level. The possibility of reducing ethylene dichloride to non-toxic acetylene provides the rationale for the development of a two-step theory of photodissociation.

The decomposition of VDC, TCE, and MC all lead to chloro or dichloroacetylene intermediates that are themselves toxic. However, these species (particularly the latter) are known to be reactive with oxygen in the ground state and are thus likely to be highly reactive in air when generated as vibrationally excited laser-decomposition intermediates. Because the nature of these laser-derived oxidation products (if any) is now known, there is a need for experiments that will identify the product species and their yield dependence on pressure, laser frequency, and fluence. Furthermore, if the organic products obtained are non-toxic or otherwise manageable, theoretical models will then be needed to interpolate yields to other non-experimental pressures and fluences.

CHEMICALS IN INDUSTRIAL USE

Any investigation of the feasibility of the laser-induced destruction of VC, VDC, TCE, ED, and MC requires a good knowledge of the industrial use of these chemicals. The chemicals we will focus on fall into two general categories: those that will be decomposed within a chemical production plant, and those that will be decomposed during their use as solvents.

VC, VDC, and ED represent the first type of chemical. VC and VDC are produced and polymerized to polyvinyl chloride and polyvinylidene chloride, respectively. ED is a precursor chemical in the production of VC. Emissions of these chemicals occur from plants where they are produced and from plants where they are polymerized. In the Los Angeles Basin, according to Air Pollution Control District regulations, emissions of VC, for example, are limited to 50 grams per hour for each plant. In VC plants, there are several reactors and dryers, and all the VC is routed to a common vent point where emissions are monitored. The proposed laser system would be positioned at this common vent point to destroy the VC before its emission to the atmosphere. Decomposition of the hazardous VC could act to lower (or prevent) emissions, or it might provide a basis for increasing VC or polyvinylchloride production while decreasing emissions from current levels. The laser system could be used in a similar plant setting to decompose VDC and ED as well.

An evaluation of the feasibility of the destruction of TCE and MC would provide an estimate of the potential for destruction of solvents in general. Both chemicals are used primarily to remove contaminants from metal parts in large industrial operations. Destruction would occur by diverting the TCE or MC diluted with air to the laser system before they are emitted from the vapor degreasing equipment.

In solvent cleaning facilities, two types of losses occur. The first is vapor emission, which includes both diffusion losses from the vapor degreaser and drag-out losses where solvent is carried out on the part. The second type of loss is the waste loss, which is "dirty" solvent that has become too contaminated for further use. Experimental data on the fraction of total solvent loss that can be attributed to each type of loss are not available. One study (OAQPS, 1977) estimated that liquid waste losses represent 5 to 20 percent of total vapor degreasing losses.[1] In another study (Palmer et al., 1980), which addressed CFC-113-based solvents, waste losses were estimated at less than 25 percent of total losses. The equipment in which CFC-113 is used is more conservative of solvent than the equipment used with other solvents because of the higher CFC-113 price. More conservative equipment would reduce vapor losses relative to waste losses, so that the 25 percent figure is probably an upper bound to the estimate of waste loss for other solvents.

Although the fraction of solvent lost through vapor emission is not known with certainty, it is safe to assume that it represents at least 75 percent of total vapor degreasing losses. This implies that greater

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[1] The waste loss in cold cleaning operations is a higher percentage of total losses.

reduction in total emission of hazardous chemicals used as solvents can be attained through preventing vapor losses than through preventing waste losses. The proposed laser system, which would be used to decompose the solvent vapor molecules, would therefore operate on the larger share of solvent emissions.

ADVANTAGES OF THE LASER TECHNIQUE

Laser-induced multiphoton dissociation offers two advantages in an industrial setting over thermal heating for decomposing the chemicals we have identified. The first of these is the selectivity of the laser. Our proposed system would operate in either a chemical manufacturing plant or an industrial production facility. Most of the candidate chemicals for destruction would be present in dilute concentration in air because of their acute danger to workers. The TLV of VC, for example, has been set at 10 ppm, whereas that for TCE is 100 ppm. With laser destruction, heat is imparted only to the VD or TCE molecules, since air does not absorb radiation in the frequency range of the CO_2 laser. The target molecules therefore absorb all of the laser radiation and dissociate. Thermal heating, on the other hand, heats the entire air stream together with the VC or TCE molecules. At a gas concentration as high as 1000 ppm, the thermal process requires 1000 times the amount of heat necessary to decompose the chemical molecules because of the presence of air. Although the CO_2 laser has a very low efficiency (between 10 and 20 percent), all of the laser energy is used to decompose the chemicals. Consequently, in dilute systems, laser irradiation can be selective, thermal heating is not, and the laser system may be more efficient on balance.

The second advantage of the laser system is that laser-induced dissociation may produce different products or products obtained only at extremely high temperatures in thermal heating. Laser irradiation of VC, for example, produces C_2H_2 (acetylene) and HCl. Pyrolysis of VC at 500° to 600° C produces chloroprene and polymeric material as well as HCl; polymeric material can cause inefficiencies in incinerators because of the tendency to cake on the walls. Only at much higher temperatures, 1500° to 2000° C, in a shock tube, are the products C_2H_2 (acetylene) and HCl obtained. The high temperatures for obtaining the more desirable products require special furnace materials and construction, making thermal destruction relatively unattractive.

In thermal dissociation, the lowest energy channel for decomposition is the one that will occur first. With a laser, rapid pumping to a higher dissociation channel is possible, and the lower channel can be bypassed to some extent. The advantage of this technique is that if a number of dissociation paths are available within a small energy range, the path that leads to the most desirable products could be chosen. This situation does not apply to the chemicals we will focus on, all of which dissociate upon irradiation by taking the lowest energy channel. It might prove useful, however, in future work where a set of non-toxic products might be preferentially selected over a set of toxic ones.

IV. SPECIFIC AIMS

This Note begins an evaluation of the feasibility of using laser-driven dissociation reactions for the emission control of noxious or environmentally threatening compounds. However, a number of specific aims need to be accomplished before the promise of the technique can be evaluated fully. These include:

1. Implement two theoretical models of multiphoton dissociation, the Lyman and Stone-Thiele-Goodman (STG) models, to allow description of one-step chloroethylene decomposition:
    - o modify Lyman theory to allow arbitrary energy eigenvalue spacings (i.e., non-SF_6 frequencies),
    - o introduce energy dependent cross-sections in the Lyman model,
    - o develop computer programs.
2. Use the multiphoton dissociation models to describe the laser decomposition of VC:
    - o determine cross-section, collisional energy transfer, and activation energy parameter values from fits to absorption data and yield-pressure-fluence data,
    - o derive unimolecular rate constants from postulated activated complexes,
    - o compare Lyman and STG results.
3. Use the Lyman and STG multiphoton dissociation models to describe the rates of decomposition of VDC and TCE:

  - parameterize the models,
  - derive unimolecular rate constants,
  - test hypothesis that intermediate chloro- or dichloroacetylene formation is the rate limiting step.

4. Perform experiments on VDC and TCE to determine the yield as a function of added gas pressure, laser frequency, and fluence:
   - in inert buffers,
   - in oxygen-containing buffers.
5. Develop a new multiphoton dissociation model that allows description of the two-step decomposition of ED and MC:
   - provide for initial excitation of the first decomposition product (e.g., excited VC from ED), and its subsequent decomposition.
6. Couple the descriptions of multiphoton dissociation with a model for a photochemical reactor:
   - select preliminary reactor geometry,
   - develop design equations,
   - estimate pressure and laser requirements for selected mass flow rates.

V. METHODS

The approach to accomplishing the specific aims involves two components. The first would be to perform a theoretical study that would involve the construction and adaptation of physically based mathematical models. The second would be to perform an experimental investigation in which fundamental multiphoton decomposition data on TCE and VDC could be obtained. The theoretical approach and the proposed experiments are synergistic. The experimental results would aid in the development of the models for describing the process of multiphoton decomposition in air and at pressures higher than generally reported in the experimental literature. The models would aid in the interpretation of the experimental data on TCE and VDC, providing a basis for predicting the two-step dissociation characteristics of MC and ED.

Details of the methods to be used are given next and follow the order of the points presented in Sec. IV, Specific Aims.

IMPLEMENTATION OF THEORETICAL MODELS OF MULTIPHOTON DISSOCIATION

To determine the requirements of a photochemical reactor, we must be able to determine the effects of pressure, fluence, gas composition, and initial temperature on the decomposition yield under arbitrary conditions. Because experimental data are not available for many combinations of these variables, it is necessary to develop or adapt a theory that will allow extrapolation from the known experimental conditions.

Fortunately several theories have been recently developed to describe the IR result in photon dissociation of polyatomic molecules, particularly the work of Lyman (1977), Grant et al. (1978), Black et al. (1977), Quack (1978), Stone and Goodman (1979), Stone et al. (1980), and Baldwin and Barker (1981). (Reviews are also available by Bloembergen and Yablonovitch (1978); Ambartzumian and Letokhov (1977); Goodman et al. (1980)).

In our application we are interested in the photochemical decomposition of organic molecules in the presence of an air buffer. Consequently, the theories we employ must include a description of the collision-induced de-excitation effects. The theories of Grant et al. (1978), Black et al. (1977), Quack (1978), Barker (1980), and Baldwin and Barker (1981) are concerned only with decomposition under collision-free conditions and therefore are only indirectly useful to us. On the other hand, the theories of Lyman (1977) and Stone et al. (1980) do include collisional effects, and these will become the molecular methodological basis for our work.

The Lyman Model of Multiphoton Decomposition

In this section, we review the theory (Lyman, 1977) and discuss how parameters may be estimated. In the next section, we will compare it to the theory of Stone, Thiele, and Goodman.

This theory presumes that molecules, having an infrared absorption band (e.g., the ν_3 fundamental in SF_6) matched to the excitation line of a laser (e.g., the 944 cm^{-1} line of the (001) to (100) 10.6 μm band in a CO_2 laser) can absorb energy in a series of steps and be promoted to the dissociation limit. It takes the effects of collision, absorption and emission of radiation, and dissociation into account and ultimately provides a prescription for the number of molecules dissociated at any time. The collisional effects are dominated by the vibrational-translational (V-T) energy transfer between excited and cold bath (e.g., argon or air buffer) molecules. (If we were dealing with pure gases at low pressures and fluences, intermolecular vibration-vibration (V-V) energy transfer would be important (Earle et al., 1978; Oref, 1981); however, we are interested in high pressures (> 50) torr with an air buffer where V-T effects are dominant.)

The absorption of energy actually occurs in two regions, a lower one where the energy eigenvalues are discrete and relatively well separated and an upper one where they are very closely spaced forming a quasi-continuum. The Lyman model describes the absorption as if all molecules were in the dense manifold of states of the quasi-continuum. Physically this means that there will always be a separation of eigenvalues equal to the energy of the photon and absorption can occur (Fermi's Golden Rule). This approximation is increasingly valid for larger polyatomics. It ignores the "bottleneck effects" that occur in up-pumping through the lower states due to the failure of the photon frequency to achieve resonance with the anharmonically narrowed transition frequencies.

The energy ladder of Lyman is therefore taken to consist of equally spaced levels separated by an amount ΔE (the photon energy). In general, because of anharmonicity this ΔE is greater than the spacing of vibrational eigenvalues; hence each level i is degenerate with the number of states g_i given by the density of states function $N(E_v)$ integrated over ΔE, i.e.,

$$g_i = \int_{E_i}^{E_i+\Delta E} N(E_v)\,dE_v \approx N(E_i + \tfrac{1}{2}\,\Delta E)\;\Delta E \qquad (5.1)$$

$N(E_v)$ can be approximated by the Whitten-Rabinovitch (1963) formula. (Lyman gives this density for 15 compounds in the energy range 0 to 50,000 cm^{-1} in Lyman et al. (1981).) The formula depends only on the known fundamental vibrational frequencies and the vibrational degrees of freedom.

The rate of change of population density in each energy level n_i is described by the energy-grained master equation (a stochastic differential equation):

$$\frac{dn_i}{dt} = \underbrace{\sum_j L_{ij} n_j - n_i \sum_j L_{ji}}_{\text{absorption and emission of radiation}} + \underbrace{\omega \sum_j P_{ij} n_j - \omega n_i}_{\text{collisional transitions}} - \underbrace{k_i n_i}_{\text{decomposition}} \tag{5.2}$$

where the meaning of the terms is indicated and

L_{ij} denotes the rate of transition of a molecule from level j to i due to the absorption ($j < i$) or emission ($j > i$) of radiation,

ω is the collisional frequency,

P_{ij} denotes the probability that a collision involving a j-level molecule will cause its transition to the i-level, and

k_i is the unimolecular rate constant for decomposition in the ith level.

Both the radiation transition rates L_{ij} and the collisional transition probabilities P_{ij} are limited to nearest neighbor transitions. In principle, all pairs of levels are connected but in a later paper, Quack

(1978) indicated that only the (radiative) transitions between adjoining levels are significant. In this case the master equation becomes

$$\frac{dn_i}{dt} = \left(L_{i,i-1} + \omega P_{i,i-1}\right) n_{i-1} + \left(L_{i,i+1} + \omega P_{i,i+1}\right) n_{i+1} - \left(L_{i+1,i} + L_{i-1,i} + \omega P_{i+1,i} + \omega P_{i-1,i} + k_i\right) n_i \tag{5.2a}$$

The Lyman evaluations of the coefficients are briefly as follows:

The collision rate ω is taken as the hard sphere collision rate using the hard sphere collision diameters determined from viscosity or virial data (Hirschfelder et al., 1954). Specifically, for the collision of the absorbing molecule A with a buffer molecule B it is

$$\omega_A = d_{BA}^2 \left(\frac{8\Pi}{\mu_{BA}\, RT}\right)^{\frac{1}{2}} P_A \tag{5.3}$$

where $d_{AB} = 1/2(d_B + d_A)$, d_B is the hard sphere diameter species B, μ_{BA} is the reduced mass, and P_A is the partial pressure of A. If the buffer gas is a mixture (e.g., air), then ω is given by the sum of all ω_A's. Equation (5.3) is important for our application because it is where we can introduce variable operating pressures.

The radiation transition rates are taken as

$$L_{ij} = \begin{cases} \sigma_i \; I/\Delta E & j = i-1 \\ \frac{g_i}{g_j} L_{ji} = \frac{g_i}{g_j} \sigma_j \; I/\Delta E & j = i+1 \\ 0 & |i-j| \neq 1 \end{cases} \tag{5.4}$$

where I is the laser intensity and $\sigma_i = \sigma(E_i)$ is the microscopic cross-section for a molecule with energy E_i. Lyman further took σ_i to be a constant for all levels (finding it necessary to reduce this value to about 1 percent of the low intensity cross-section σ_{01} to account for observed reaction rates in the SF_6 system). Microscopic reversibility was used to derive the second line of Equation 5.4 from the first. The g_i factors appearing in the $L_{i,i+1}$ case arise because of the presence of various modes and the assumption of a rapid intramolecular V-V redistribution of energy (generally occurring on the psec time scale while the laser pulses are on the order of 100 nsec (Bloembergen and Yablonovitch, 1978)).

Lyman estimated the dissociation rate constants, k_i, from RRKM (Rice-Ramsperger-Kassel-Marcus) unimolecular reaction rate theory (Robinson and Holbrook, 1972). To take the energy graining into account

$$k_i = \frac{1}{\Delta E}\int_{E_i}^{E_i+\Delta E} k_a(E^*)dE^* \approx k_a(E_i+\Delta E/2) \qquad (5.5)$$

where $k_a(E^*$ is the RRKM rate constant for a molecule of energy E^* (total vibrational energy). The RRKM model assumes that molecules undergoing decomposition must be pumped over a saddle point in the potential energy surface connecting reactant and product, the saddle point (or activation barrier) lying E_0 energy units above the reactant ground state. It further assumes that molecules pumped above the barrier (but retaining most of their ground state geometry) are in statistical equilibrium with those "activated complex" molecules of equivalent energy lying above the saddle point (and characterized by a geometric distortion along the reaction coordinate, generally one of the vibrational modes). Statistical mechanics then gives the ratio of the active molecules (the subset of n_i in Eq. (5.2) with energy E^*) to the activated complexes as the ratio of their partition functions, i.e., $n(E^*)/n_{\text{act cplx}}(E^*) = Q/Q_{\text{act cplx}}$. When the expression for $n_{\text{act cplx}}(E^*)$ is multiplied by the translational velocity across the barrier, one obtains the number of molecules crossing the barrier per unit time or the rate constant k_a:

$$k_a(E^*) = L^{\pm} \frac{Q_r^+ \sum_{E^+=0}^{E^+} P(E^+)}{Q_r h \, N^*(E^*)} \qquad (5.6)$$

where $h^{-1} Q_r^+ \, \Sigma \, P(E^+)$ is derived from the $Q_{\text{act cplx}}$ partition function, $Q_r N^*(E^*)$ is derived from the Q partition function, and L is a statistical factor giving the number of equivalent dissociation pathways. Here E^+ is the vibrational energy in excess of E_0, $N^*(E^*)$ is the density of states at E^*, $P(E^+)$ is the number of states having vibrational energy E^+ (both are expressible using the Whitten-Rabinovitch formula), and Q_r and Q_r^+ are conventional rotational partition functions.

The Lyman expression for P_{ij} is based upon a mechanism where collisions are assumed to cause only unit losses of vibrational quanta of energy from the lowest frequency mode. (For simplicity in Equations

(5.7) through (5.10), we now assume that all modes are degenerate and absorbing and that the laser photon ΔE equals the vibrational energy spacings.) The transition probability for this process is assumed to be given by the harmonic oscillator relation from which one can obtain (Wilson et al., 1955):

$$P_{i-1,i} = P_{01} i \tag{5.7}$$

where any i to i-1 transition is related to the lowest level (0 to 1) transition. Microscopic reversibility gives the upward rate for gain of quanta by collision, i.e.,

$$P_{i,i-1} = \frac{g_i}{g_{i-1}} P_{i-1,i} \exp(-E_i/kT) = \frac{i g_i}{g_{i-1}} P_{01} \exp(-i\Delta E/kT) \tag{5.8}$$

where g_i is again the degeneracy of the ith energy level. By virtue of the harmonic oscillator selection rules,

$$P_{ij} = 0 \qquad |i-j| > 1 \tag{5.9}$$

These equations demonstrate that all the collision-induced transition probabilities can be expressed in terms of a single parameter P_{01}.

A relation for obtaining P_{01} from thermal relaxation data was derived by Lyman. By multiplying Eq.(5.2) by iΔE and summing over all i, one can obtain a differential relation for the time dependence of the total vibrational energy $E = \Sigma\, n_i E_i$. The right-hand side of the differential can be re-expressed using appropriate relations for the P_{ij} (L_{ij} and k_i are zero) to obtain a first-order rate equation from which the relaxation rate ($1/\tau$) can be identified. Lyman shows this to be

$$\frac{1}{\tau} = \omega P_{01}\ [1 - \exp\ (-\Delta E/kT)] \tag{5.10}$$

or using Eq. (5.3) under the assumption of only pure or greatly diluted absorber being present,

$$\frac{1}{P\tau} = d_{AB}^2 \left(\frac{8\Pi}{\mu_{AB} RT}\right)^{\frac{1}{2}} P_{01}\ [1 - \exp\ (-\Delta E/kT)] \tag{5.11}$$

where P is the partial pressure of the gas in excess. This form is particularly useful, since the constant product $P\tau$ is obtainable from shock-tube, ultrasonic, or spectroscopic experiments for various buffer gases.

In summary, Eqs. (5.1) through (5.9) constitute the Lyman model. The coefficients of the Lyman model have now been defined in some detail. From them one can determine that the Lyman model depends primarily on three parameters:

P_{01} (lowest level collision transition probability),
σ (cross section),
E_0 (the activation barrier height),

and on the assumed geometry of the activated complex. E_0 is available for a large number of compounds from the kinetic analyses of thermal data (e.g., Robinson and Holbrook, 1972; Benson, 1960). An estimate for P_{01} can often be obtained from shock-tube, ultrasonic, double resonance

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or infrared fluorescence relaxation data (e.g., Bott and Jacobs, 1969; Steinfeld et al., 1970; Moore, 1969). These references summarize their results in the form of an empirical $P\tau$ = constant relation (where P is pressure and τ is the overall relaxation time); Eq. (5.11) provides a prescription for relating this $P\tau$ to P_{01}. As employed by Lyman, the multiphoton cross-section must be treated as a free parameter because the macroscopic cross-section σ is not equal to the low intensity cross-section σ_{01} (i.e., principally the $v = 0$ to 1 transition) available in the literature. (Estimation of these parameters for the particular case of VC is deferred until after the Stone-Thiele-Goodman model is reviewed.)

The Stone-Thiele-Goodman (STG) Model

The STG model is presented in Stone et al. (1980). These authors begin their derivation from the time dependence of the full density matrix but show that under the assumption of incoherent pumping through the quasi continuum that it reduces to the same energy-grained master equation (EGME) given in Eq. (5.2). Laser pumping of the molecules through the low lying, discrete energy states is generally not incoherent but Stone et al. show that at high buffer gas pressures (> 100 torr), rapid rotational hole filling allows one to ignore this and use only the EGME.

The coefficients of STG assume different forms than those used in the Lyman model. While the collision frequency (ω) remains the same, the collision transition probabilities P_{ij} change. Specifically the probability for a down transition is taken as

$$P_{ij} = \alpha \exp\left[-\beta(E_j - E_i)\right] \tag{5.12}$$

Unlike the Lyman model, Eq. (5.12) allows transitions to occur beyond nearest neighbor states; however, β is quite large (Table I of Stone et al., 1980) and consequently the probabilities drop off very rapidly with increasing energy gap. Because

$$P_{jj} = 1 - \sum_{i=j} P_{ij} = \alpha$$

α can be obtained in terms of β. β can be used directly as a relaxation parameter, or equivalently, can be related to the mean energy η transferred upon collision to a cold heat bath according to

$$\eta = h\nu/[\exp(\beta h\nu)-1] \qquad (\nu = \text{laser frequency}) \tag{5.13}$$

As in the Lyman model, probability for the up transition can be obtained from microscopic reversibility as

$$P_{ij} = P_{ji} \frac{g_i}{g_j} \exp\left[-(E_i - E_j)/kT\right] \tag{5.14}$$

where g_i is the level degeneracy factor and T is the temperature of the buffer gas (ambient in our applications).

Instead of using the Whitten-Rabinovitch (1963) formulas to determine g_i, Stone et al. (1980) used a simpler approach. They modeled the actual vibrational energy ladder as having s-fold degenerate rungs separated by an energy gap given by the arithmetic mean $<\nu>$ of the s fundamental frequencies. The density of states $\rho(s,n)$ was calculated for this model from the statistical degeneracy factor at the nth rung

$$g(s,n) = \frac{s + n-1}{(s-1)!n!} \text{ as } \rho(s,n) = \frac{g,(s,n)}{h<\nu>}$$

$\rho(s,n)$ was then generalized to a continuum function via the introduction of gamma functions and n was replaced by $(ih\nu)/(h<\nu>) = i\nu/<\nu>$ to match the actual energy ladder to the laser absorption ladder. The g_i (referring to the laser absorption ladder) is then

$$g_i = h\nu \ \rho(s,i\nu/<\nu>) \tag{5.15}$$

The reaction rate k_i is given by either the quantum RRK theory (Robinson and Holbrook, 1972) or the RRKM theory following the discussion above for Lyman.

The laser absorption rates L_{ij} differ considerably between the Stone et al. and Lyman theories. An expression for this rate is:

$$L_{ij} = \frac{<\alpha^2>_{ij} \ A^2}{2\hbar^2} \left(\frac{1}{T_2}\right)_{ij}^{-1} \qquad - = j \pm 1 \tag{5.16}$$

which is simplified from a more complete Lorenztian line shape factor derived for a homogeneously broadened dipole transition where A is the amplitude of the laser field, $(1/T_2)_{ij}$ is the intramolecular relaxation rate, and $<\alpha>_{ij}$ is a harmonic oscillator transition element averaged over all the i(j < i) or or i + 1 (j > i) pump mode levels capable of transitioning into a fixed pump mode plus bath mode energy level E_i (Stone and Goodman, 1979).

In several papers (Stephenson et al., 1979; Stone et al., 1980), it was shown that $1/T_2$ depends on the energy levels involved and that

$$\left(\frac{1}{T_2}\right)_{ij} = \frac{2\pi\, H_{an}}{\hbar}\left(\rho_i^{sqe} + \rho_j^{sqe}\right) \tag{5.17}$$

where H_{an} is a free parameter expressing the ability of the anharmonic interaction between intramolecular vibrational levels to lead to single quantum energy exchanges and ρ_i^{sqe} is the density of quantum states constrained to total energy E_i and to single quantum exchanges. Stone et al. (1980) give

$$\rho_i^{sqe} = \frac{s(s-1)}{h<\nu>}\,\frac{(E_i/h<\nu>)^2}{(E_i/h<\nu> + s-1)(E_i/h<\nu> + s-2)} \tag{5.18}$$

where the variables have all been defined previously.

Thus, substituting Eq. (5.17) and Eq. (5.18) into Eq. (5.16), the final STG expression for L_{ij} is obtained:

$$L_{ij} = \frac{2<\alpha^2>_{ij}\, I}{\hbar\, H_{an}^2\, c\left(\rho_i^{sqe} + \rho_j^{sqe}\right)} \propto \delta\,\frac{I}{\rho_i^{sqe} + \rho_j^{sqe}} \tag{5.19}$$

where A has been replaced by its corresponding intensity and where the coefficients have been grouped into a single parameter δ.

In summary, the STG theory is given by Eqs. (5.12) through (5.15) and (5.17) through (5.19). The parameters not identified by molecular or known initial conditions are of the same number as in the Lyman theory, namely, the three parameters η (or β), E_0, δ. If RRKM theory is used, then the geometry of the activated complex is also required. Like the parameterization of the Lyman theory, E_0 is generally known or can be estimated from thermal decomposition experiments, leaving η and δ as the principal free parameters.

APPLICATION TO VINYL CHLORIDE--ESTIMATION OF PARAMETERS

Either the Lyman or STG theories can be applied to vinyl chloride, although the STG theory is less phenomenological in its treatment of light absorption. We intend to use the STG theory but will draw on the Lyman procedure for establishing a relation between η and the experimental $P\tau$ values. We will also rely on it for backup. Significant guidance in the application of STG theory is available in Stone et al. (1980) where it was applied to describe the buffer pressure (0 - 700 torr) and fluence dependence of the dissociation of the halogenated ethylene CF_2CFCl.

To apply the theories to VC, we only need to show that the parameters can be estimated. In either theory, there are three parameters to consider: E_0, P_{01}, σ (Lyman); E_0, η, δ (STG). E_0 for VC has already been estimated from thermal data as 69.3 kcal/mole (Reiser et al., 1979). P_{01} and η both refer to collisional relaxation and can be obtained from $P\tau$ values (via Eq. (5.11) for $P\tau$). The $P\tau$ value ultimately of importance to us describes the rate of VC vibrational relaxation in the presence of air.[1] Literature values are available only for VC self relaxation (Fogg and Lambert, 1955) or for VC rotational relaxation in a helium buffer (Lussier et al., 1978), but these can be supplemented with correlations between vibrational relaxation times of other species with various buffers to assess values for vinyl chloride-nitrogen (Moore, 1965; Millikan and White, 1963). In particular, the correlation of Millikan and White

$$\log_{10}(P\tau) = 5 \times 10^{-4} \mu^{\frac{1}{2}} \theta^{\frac{4}{3}} [T^{-\frac{1}{3}} - 0.015\mu^{\frac{1}{4}}] - 8.00 \tag{5.20}$$

may prove useful in estimating τ. Here μ is the reduced mass and θ is the characteristic temperature of the lowest frequency oscillator in °K. The relaxation time for a species A in a binary mixture (τ_{mix}) is given by the weighted sum

$$\frac{1}{\tau_{mix}} = \frac{P_A}{P\tau_{AA}} + \frac{P_B}{P\tau_{AB}} \tag{5.21}$$

where P_i/P is the mole fraction of i, τ_{AA} is the self-relaxation time, and τ_{AB} is the relaxation time of species A with buffer B.

The parameters σ (or σ_i if allowed to vary with energy level) (Lyman) and δ (STG) both refer to the microscopic radiation absorption

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[1] The relaxation times of oxygen and nitrogen are of the same order of magnitude (Cottrell and McCoubrey, 1961). Furthermore, their fundamental absorption bands, as well as that of water, lie far enough above the chloroethylene laser frequencies to rule out significant attenuation of the laser beam. On the other hand, carbon dioxide in air is perfectly matched to the CO_2 laser, but the low concentration of the gas in air coupled with the low population of the excited absorbing state also prevents significant attenuation.

characteristics of a molecule. They can be obtained from the experimental VC absorption data in Lussier et al. (1978) (Fig. 2) (also in Lyman et al., (1981) (Fig.5)) in which the number of photons absorbed per molecule during a pulse in a focused sample of known geometry[2] is plotted as a function of 2 to 3 orders of magnitude of fluence. Because of their microscopic nature, the σ and δ parameters cannot be obtained directly from the data but rather require that Eqs. (5.2) (modified to take the sampled geometry into account and with $k_i = 0$ and other parameters selected) be solved, and the absorption per molecule derived from it be iteratively fit to the data. To minimize the effects of rotational hole filling and to avoid using the STG theory modified to include this effect (Stone et al., 1980, p. 2264), one should fit to the vinyl chloride absorption data taken in the presence of the highest buffer pressures (40 torr) where collisions tend to overcome this problem.

In a more detailed study, the methods for integrating Eq. (5.2) would be numerical. To avoid difficulties in solution due to the occurrence of stiffness, either the Gear method (Gear, 1971; IMSL, 1977) (already used successfully by Lyman (1977) and Baldwin and Barker (1981)), or perhaps the Monte Carlo method of Gillespie (1976, 1977) (already used successfully by Barker (1980)) might be used. In addition, for the correct form of the coefficients, there is some possibility that the stochastic master equations might be integrated analytically for the first moments of the fractional yield distribution as a function of fluence. Baldwin and Barker (1981) have already accomplished this for the case of collisionless conditions suggesting that such an approach might be used here.

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[2] Sample cell geometries and focusing lens specifications are included in Lussier et al. (1978).

PHOTOCHEMICAL DECOMPOSITION OF VINYLIDENE CHLORIDE AND TRICHLOROETHYLENE

We have described our approach for the theoretical investigation of vinyl chloride decomposition. In this subsection, we present a similar discussion of a theoretical approach for examining the photochemistry of the other toxic members of the chloroethylene series, VDC and TCE.

Products

We begin with an expanded characterization of the reaction products obtained from VDC and TCE. First, published data (Reiser et al., 1979; Nagai and Katayama, 1978) have shown that chloroacetylene and dichloroacetylene are the principal reaction products in the absence of air, yet dichloroacetylene is the more reactive and is explosive at 1.0 atm (Reiser et al., 1979; *Handbook of Chemistry and Physics*, 1967). Because we will ultimately be considering the destruction of chlorocarbons in air, these observations raise the question of whether the highly excited chloroacetylenes formed under laser action will spontaneously react with oxygen and yield other products. This question is difficult to resolve theoretically, so we suggest an experimental approach in which decomposition is carried out in the presence of oxygen and non-acetylenic products are sought in the mass spectral data (see the next subsection).

Second, if oxygen has no effect (or only dichloroacetylene is oxygen sensitive) and the chloroacetylenes are the only reaction products, methods for their treatment would have to be considered in more detail. For example, while it is known (Beilstein, 1958) that water will decompose the chloroacetylenes at ambient temperatures, the rates of their dissolution in water (e.g., transport into a film of water) and subsequent reaction must still be estimated to assess whether a scrubber based on this chemistry would be feasible. If only the dissolution rate is fast enough, then the option of direct discharge into water could be evaluated.

Modeling

If air acts as an inert buffer in the decomposition of VDC and TCE, then the combined MPD-reactor model (either Lyman or STG dependent) could be used to estimate laser requirements, operating pressures, and yields as outlined previously for vinyl chloride. If oxygen proved to be a reactant, then the model could still predict the yield, provided passage over the chloro or dichloroacetylene barrier is the rate limiting step (i.e., the overall reaction coordinate passes through the chloroacetylene activated complex and then proceeds downhill). For the case of reactive oxygen, an STG model calculation for the conditions of the experiments could be performed. If the measured yields were reproduced in the model, it would be possible to verify whether chloroacetylene formation is the rate limiting step.

The multiphoton dissociation parameters E_0, P_{01}, σ (or σ_i) in the Lyman model or E_0, η, δ in the STG must be estimated for VDC and TCE. Reiser et al. (1979) have estimated the E_0 activation barrier for the elimination of HCl from vinyl chloride and TCE at 69 kcal/mole. Because VDC is the intermediate analog, it might be assumed that it has the same barrier. P_{01} (or η) could again be estimated from thermal relaxation rates (or chemical activation data); $P\tau$ values can be estimated for the chloroethane -N_2-O_2 system from the Millikan and White (1963) correlation as noted earlier.

The estimation of σ_i or δ is more difficult for VDC and TCE than for vinyl chloride because extensive absorption vs fluence studies have not yet been performed. Reiser et al. (1979) have investigated their decomposition only at one pressure and wavelength, ascertaining that dehydrohalogenation is the primary pathway.

An approximate procedure based upon observations of Lyman et al. (1981) could be adopted. They noted that the functional relationship between the number of photons per molecule absorbed from an intense field $\langle n \rangle$ and the product $\sigma_0 \Phi$ (Φ is fluence) falls into two groups. The ethylenic compounds they considered (ethylene and vinyl chloride) fall into the same group and have approximately the same functional relationship. Initially, it could be assumed that VDC and TCE share this relationship, i.e., that the σ_0 is a suitable normalization constant. (Lyman et al. also present a more refined correlation, but it is model dependent and it is not clear that the parameters could be obtained for the chloroethylenes.) The approximate $\langle n \rangle$, $\sigma_0 \Phi$ relationship, could be fit to the $\langle n \rangle(\Phi)$ relation[3] obtained from the STG model to obtain δ. If the Lyman model were used, one would probably not solve for a constant σ but rather would solve for a parameter in an energy dependent cross-section, e.g., the q in $\sigma = \sigma_{01}(E_i/E_1)^q$ where q is generally negative (Barker, 1980; Baldwin and Barker, 1981). The indicated behavior of a microscopic cross-section that increases with i

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[3] For a constant intensity absorption experiment,

$$\langle n \rangle = \frac{1}{N_t} \sum_j \int_0^{t_p} L_{ij} n_j(t)\,dt, \quad j < i$$

where N_t is the total number of absorbing molecules and t_p is the pulse length. If net absorption is considered, then emission L_{ij}^p's must also be included.

has already been demonstrated as implicit in the STG model (Stone et al., 1980) so no similar modifications of δ are necessary.

Once the multiphoton dissociation model was fully parameterized, it could be used to estimate the decomposition yield of VDC and TCE under various laboratory conditions as a function of pressure and fluence. The exact laboratory sample geometries, focusing conditions, pulse length, etc., could be chosen in collaboration with an experimental laboratory. The results of yield and absorption experiments on these compounds (see the next subsection) could then be used to test the validity of the model predictions and to effect refinements of the model parameters.

EXPERIMENTS

The experiments necessary for the detailed analysis are as follows:

(a) Measurements of the pressure and fluence dependence of the multiphoton IR absorbance and decomposition yields of vinylidene chloride and trichloroethylene.

(b) Identification of the products obtained from VDC and TCE when nitrogen and when air (oxygen) buffer gases are present during decomposition.

Experiment (a) is aimed at characterizing the chloroethylene analog behavior of absorption and molecular energy transfer parameters. Experiment (b) is aimed at determining whether the excited chloroacetylene products (especially at high fluence) react with ground state oxygen.

Both pressure and fluence variables should be spread over a wide range, but the pressure range might generally be restricted to 50 torr and higher to avoid the complications of rotational hole filling in analysis of the results. Beam profiles and focusing optics could be determined to allow accurate characterization of the reaction volume and the fluence within it. Because this reaction volume is a small fraction of the total sample cell volume, multiple pulses could be passed through it to produce sufficient product for analysis by mass spectrometry and infrared spectroscopy.

TWO-STEP DISSOCIATIONS

Earlier we discussed the experimental results for the multiphoton dissociation of methyl chloroform. The products are CH_2CCl_2 (VDC) and HCl in the first decomposition step and C_2HCl (chloroacetylene) and HCl in the second step. Although no experimental data are available for the second step of the dissociation of ED, we suspect that this molecule would behave analogously to methyl chloroform. The first step yields C_2H_3Cl (VC) and HCl, while the second is likely to result in C_2H_2 (acetylene) and HCl. A more detailed analysis would involve theoretical work on both MC and ED. Using the models described earlier, together with the experimental data on MC, ED, VC, and VDC, the two-step dissociation process could be investigated. This work would culminate in parametric estimates of the dissociation product yields for MC and ED. Below we describe an approach to this analysis.

Although MC has been studied in three different laboratories (Preiswerk et al., 1979; Nagai and Katayama, 1978; Sudbo et al., 1978b), experimental evidence for the two-step decomposition process is provided in only one study (Sudbo et al., 1978b). This group used the crossed laser and molecular beam method to accomplish decomposition. Methyl chloroform has a C-C stretching vibration at 1075 cm^{-1} and a C-H rocking vibration at 1084 cm^{-1}. The exciting CO_2 laser frequency used was the R(12) line of the 9.6 μm band, at 1073.3 cm^{-1}. The first step in the four center dissociation was reported to be HCl elimination, which is indeed the lowest energy channel. The group also observed a weak, broad background in the velocity distribution of the HCl, which is interpreted to imply secondary dissociation of CH_2CCl_2 (VDC) to C_2HCl (chloroacetylene) and HCl. The detected CH_2CCl_2 is reported to be vibrationally excited and further decomposition occurs readily. The CH_2CCl_2 molecule has an absorption band at 1095 cm^{-1}, which does not coincide with the laser frequency used in the first dissociation step. Nevertheless, apparently because the CH_2CCl_2 molecule is in a vibrationally excited state, the energy supplied by an off-resonance source is sufficient to cause dissociation. Thus, we have evidence, in the case of MC, that even though the exciting frequency for the first step is far from optimum for the second step, two-step decomposition occurs.

The crossed laser and molecular beam arrangement of Sudbo et al. (1978b) allows the direct measurement of the translational energy distribution of the dissociation fragments. The total excess energy of these fragments must be partitioned among the translational, vibrational and rotational degrees of freedom. The result of this experiment, which included other molecules in addition to MC, was that less than about 15 percent of the total excess energy is released in translation. This implies that at least 85 percent of the excess energy is available as internal energy (vibration and rotation).

To establish a quantitative basis for discussion, we present the energy level diagram for the two-step decomposition of MC in Fig. 5.1.

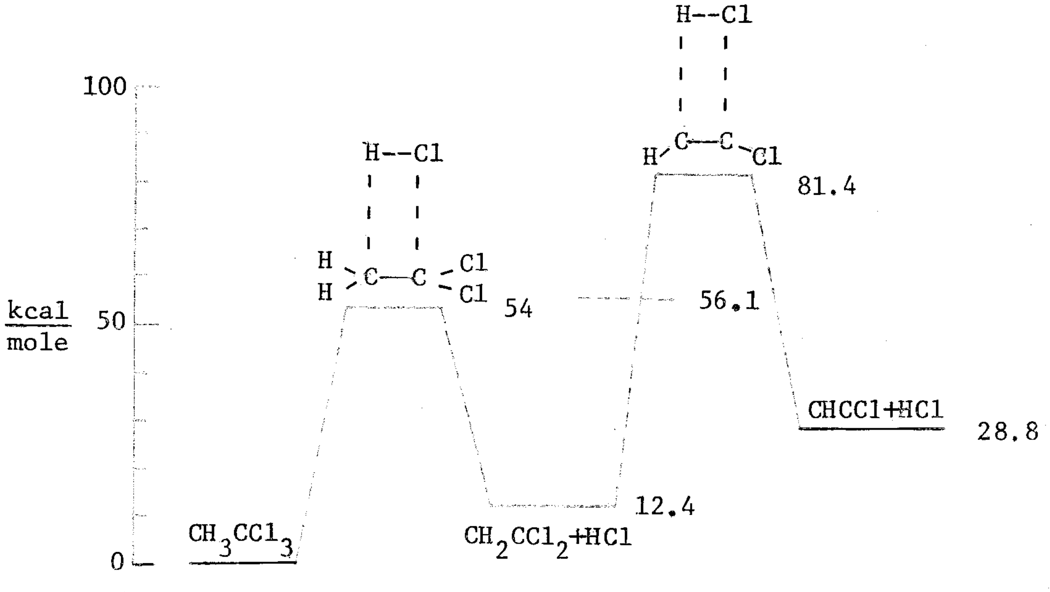

Fig. 5.1 -- Energy Level Diagram for Two-Step Dissociation of Methyl Chloroform

Data for the first step of the decomposition were taken from Sudbo et al. (1978b), and data for the second step were estimated according to assumptions that will be outlined shortly. The second step of the dissociation reaction takes place in a different reaction coordinate from the first step. Although it is not strictly correct to do so, we show the two steps on the same reaction coordinate in Fig. 5.1 simply for convenience.

There are no available data on the energy of activation of VDC for the second step of the dissociation process. One study (Reiser et al., 1979) does report a thermal activation energy of about 69 kcal/mole for the HCl elimination in VC and TCE. Because we have no data for VDC, we will assume this value for VC. Indeed, there is some evidence that members of an analog series have activation energies that are in the same range. For example, the energies of activation of C_2H_5Cl (ethyl chloride) and CH_2ClCH_2Cl (1,1-dichloroethane) for HCl elimination taken at various temperatures average about 58 and 50 kcal/mole, respectively (Benson and O'Neal, 1970). These two values, together with the value for MC of 54 kcal/mole (Sudbo et al., 1978b), illustrate that activation energies for HCl elimination from these three members of a series do not differ significantly. It therefore seems reasonable to assume a value of 69 kcal/mole for VDC; this is indicated by the horizontal line at 81.4 kcal/mole in Fig. 5.1. The heat of formation of C_2HCl (chloroacetylene) is apparently not known. However, using data from Benson (1960), we have estimated that the formation of this molecule lies in the range of 28.8 ± 6 kcal/mole on the scale of Fig. 5.1.

In the first dissociation step, the barrier to back reaction is 42 kcal/mole. Sudbo et al. (1978b), in an RRKM calculation, have determined that the excess energy above the dissociation threshold corresponding to a 10 ns lifetime is 22 kcal/mole. In other words, MC is excited 22 kcal/mole above the dissociation level during the experiment. The total excess energy available to the decomposition products is the sum of these two energies, or 64 kcal/mole. Sudbo et al. report an average translational fragment energy of 8 kcal/mole, or 12.5 percent of the total excess energy. This leaves about 56 kcal/mole to be partitioned among the internal degrees of freedom of the fragments. For current purposes, we will assume that this energy can be apportioned according to the principle of equipartition of energy. The CH_2CCl_2 fragments therefore have 3 degrees of rotational freedom and 12 degrees of vibrational freedom; the HCl fragments have one rotational and one vibrational degree of freedom. Therefore, the CH_2CCl_2 molecules possess about 88 percent of the total available energy, or 49.2 kcal/mole. Rotation accounts for approximately 5.5 kcal/mole leaving 43.7 kcal/mole as vibrational energy. The dotted line at 56.1 kcal/mole (43.7 kcal/mole + 12.4 kcal/mole) in Fig. 5.1 shows the approximate location of the excited CH_2CCl_2 fragments immediately after the first dissociation step.

From these data, it is apparent why the non-coincidence of the exciting laser frequency (1073.3 cm^{-1}) and the vibrational frequency of the CH_2CCl_2 molecule (1095 cm^{-1}) do not seriously hinder the second-step decomposition. This decomposition from an excited vibrational state (at 56.1 kcal/mole) requires energy input of about 24.3 kcal/mole to surmount the activation barrier, which is significantly less than the 69 kcal/mole required for decomposition from the ground vibrational state.

It should be emphasized that some of the data used to construct Fig. 5.1 are preliminary and in a complete study we would gather more accurate information. This especially applies to the energy of activation of CH_2CCl_2 and the heat of formation of C_2HCl. Nevertheless, Fig. 5.1 adequately illustrates the qualitative picture for the two-step dissociation of MC. A similar representation of the dissociation of ED could be constructed. In that case, although there is no experimental verification, we also presume that the fragments from the first dissociation step are vibrationally excited. The laser excitation frequency of the first step of the ED decomposition is 944.2 cm^{-1}; the C_2H_3Cl molecule produced in this dissociation has a vibration at 940 cm^{-1} (Wu, 1946). These two frequencies lie much closer than those of the exciting frequency and the vibrational frequency of CH_2CCl_2 in the MC case; it is therefore even more reasonable to assume that the second step will occur in the decomposition of ED.

Experimental work on MC or ED might not be necessary for a more detailed study. Dr. J. Steinfeld of MIT, in a private communication, has indicated that his group will shortly begin a series of experimental studies on the chloroethane series. It is possible that some of the results obtained in that work could be useful.

Further work would involve predicting from theory the product yields that can be expected for the second dissociation step in both molecules. The existing experimental data (Preiswerk et al., 1979; Sudbo et al., 1978b; Nagai and Katayama, 1977), any new experimental results that are obtained (Steinfeld), and the refinements of model parameters described earlier could be used as the basis for a theoretical investigation. The theoretical work on ED would depend, to some extent, on the results of an analysis of the chloroethylene series. If the behavior of each member of that series proved to be similar or uniform, then there would be a basis for assuming that MC and ED, both members of the chloroethane series, would exhibit analogous behavior. Since no data on the second step of the ED dissociation exist, dissociation of the molecule can be accurately characterized theoretically only if patterns within analog series emerge.

Again, in the case of MC and ED, the multiphoton dissociation parameters E_0, P_{01}, σ (or σ_i) in the Lyman model or E_0, η, and δ in the STG model could be estimated. For E_0, the energy of activation of MC we could use 54 kcal/mole (Sudbo et al., 1979). Because there is evidence that activation energies do not vary significantly among members of the same analog series, the same value might be adopted for ED. For the activation energy of the second step of the decomposition (VC and VDC dissociation), the value 69 kcal/mole could be used, as discussed earlier in this section. P_{01} (or η) for MC and ED in the first step decomposition could be estimated from thermal relaxation rates, and the $P\tau$'s might again be estimated from the Millikan and White (1963) correlation. The estimates of P_{01} for VC and VDC described earlier could be used to characterize the second step of the dissociation.

We have no experimental data for estimating σ (or δ) for MC or ED verifying the $\sigma_0\Phi$, $<n>$ relationship. Steinfeld has indicated in a private conversation, that he intends to obtain these data for at least one member of the chloroethane series; if these data were available, σ (or δ) could be estimated under the assumption that there is not much variation among members of a series. If these data were not available, two different approaches, both of which are only approximations, might be employed. The first approach would be to simply adopt the σ (δ) estimates for the chloroethylene series. The second would be to assume that σ is constant over all fluences. This is tantamount to assuming that Beer's law can be used to describe the dissociation of MC and ED. Indeed, there is some evidence that molecules with more than seven atoms dissociate in the fluence range for linear absorption (Lyman et al., 1981). In this case, a value for σ ($= \sigma_{01}$) could be simply obtained from the literature. For the second step of the dissociation, involving VC and VDC, the method outlined earlier for estimating σ (or δ) could be used.

It is important to account for the fact that the products obtained in the first dissociation step (VC and VDC) are vibrationally excited.

From the experimental data of Sudbo et al. (1978b), the degree of vibrational excitation in the case of MC can be ascertained under the assumption of the equipartition of energy. Although no experimental data on ethylene dichloride are available, given similarities among members of analog series, it would not be unreasonable to assume that the first-step product, VDC, has approximately the same vibrational energy as VC obtained in methyl chloroform dissociation.

Using these parameters in the model, the yields of the final products of the two-step dissociations could be theoretically determined for various fluences. This would allow a prediction of the fluence at which 100 percent decomposition can be obtained.

PRELIMINARY DESIGN CONSIDERATIONS

The purpose of the detailed theoretical and experimental investigation described earlier is to gain insight into the physics of the infrared multiphoton dissociated process at various buffer gas, fluence, and pressure conditions. The constraints of a system for treating an actual waste stream must include a provision for total mass flow. In this section, we show how a proposed reactor system integrates the characteristics of mass flow with the earlier decomposition theories.

In a detailed study, it would be necessary to provide guidance on operating pressures and laser characteristics for the design of a chemical reactor. To satisfy ourselves that a simple decomposition system could be assembled using a state-of-the-art laser and vacuum system, we have performed an initial assessment of reactor characteristics. While we recognize that the laser and vacuum system are not the only components contributing to the cost of a reactor, we believe they represent a large fraction of the total system cost.

Below, we present a potential reactor system and discuss some important features that must be addressed in specifying the reactor parameters and costs.

Photochemical Reactor

To determine the requirements of a laser used to decompose hazardous chlorocarbons in an actual setting, a complete photochemical reactor must be considered. This is because incident intensity, pulse rate and average power are determined not only by molecular properties and pressures (as treated in the Lyman or STG models) but also by gas flow rates and the optical design of the reaction chamber. Furthermore while the costs of a photochemical control system depend on the laser(s) used, they also depend on vacuum pumps, scrubbers, and the like.

In this subsection, we therefore present a very preliminary reactor design useful for destroying solvent vapors being lost in a process waste stream or from a vented holding tank. In the next subsection, we present simplified design equations for a specific application and perform a sample calculation to demonstrate both the design considerations involved and the potential technical feasibility of photochemical emission control.

In Fig. 5.2 we present a simplified drawing of the laser control system. We assume that the inlet stream consists of air containing solvent at a low concentration (on the order of 1000 ppm, such as might be encountered in a flow stream previously regulated to maintain a TLV in the workplace). A reducing valve and rotary pump are shown because they may be required to keep pressures in the reaction chamber low enough to prevent significant collisional losses of energy from the

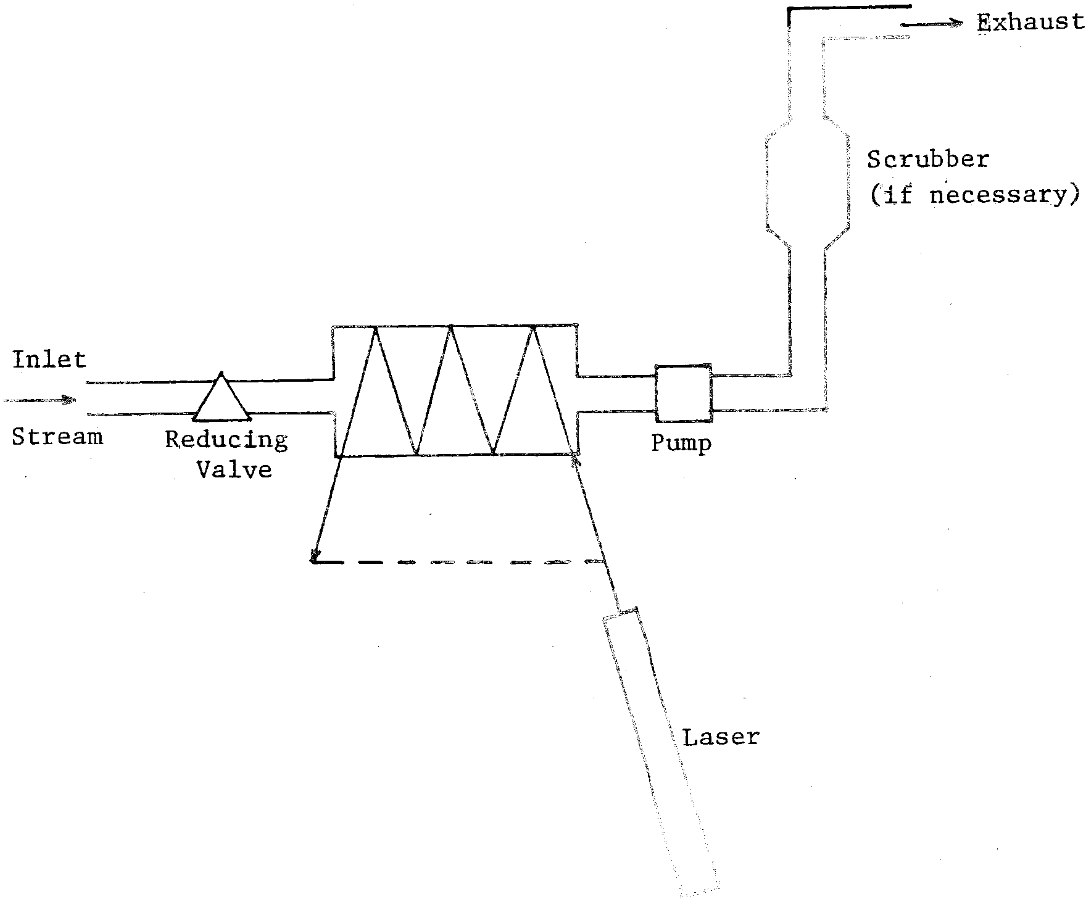

Fig. 5.2 -- Laser Control System

absorbing molecules. The reaction chamber is shown as a flat entity with mirrored surfaces on either side reflecting the light beam and creating a long optical path. For IR dissociation the light would be emitted from a carbon dioxide laser. For those cases where the photochemical reaction produces chlorine or chloroacetylenes, an alkaline water wash scrubber will also be required. For vinyl chloride, where the emphasis lies on the removal of carcinogenicity from the product stream, the non-carcinogenic HCl and acetylene products (if < 800 ppm) may be exhausted to the air without scrubbing.

Configurations other than that shown in Fig. 5.2 are possible and probably desirable. One modification, for example, might consist of routing the exit beam back to the entrance (denoted by the dotted line in Fig. 5.2) to reduce the laser power requirement. Other modifications might include the employment of multiple lasers on large flow systems, or redesign of the section chamber optics to reduce the number of beam reflections.

Specification of the Photochemical Reactor Parameters

The principal element of the system design involves determining the required characteristics of the laser and pump. Feasibility of the system is possible only if the average power, pulse rate, and pulse length of the laser and the pumping rate are physically and economically accessible. In this subsection, we present and solve greatly simplified design equations that demonstrate most of the factors that must be considered when determining these parameters. *These equations do not include the multiphoton dissociation (MPD) models presented earlier, but should be integrated with them if future work is undertaken.* In particular, the concept of a simple reaction threshold used below could be replaced by the RRKM (or QRRK) formulation discussed above; and the intensity would have to become both spatially and time dependent because of the thick absorbing layers. *The principal benefit of a combined MPD-reactor model would be to provide us with a method for determining the power and vacuum requirements for any pressure of buffer gas* (i.e., air). In the example that follows, we have assumed that the operating pressure must be lower than ambient, about 0.1 atm, to greatly reduce collisional effects (Stone et al., 1980). The reactor would be simpler and cheaper, however, if we could operate at higher pressures, but this will come at the cost of a several-fold increase in intensity, the exact value of which can only be derived from the combined MPD-reactor model.

An Example System Parameterization

Details of a possible idealized reaction chamber design are shown in Fig. 5.3. It is a slot open on both ends to allow a low-level gas flow across the area A. A simple practical design would have two of the side surfaces mirrored to allow multiple reflections and a long path length as indicated in Fig. 5.2. However, for ease of calculation, we show the light beam in Fig. 5.3 turning right angles at the edges so that it traverses a series of parallel paths, eventually exiting the chamber and entering a light trap. Each traverse of the light beam

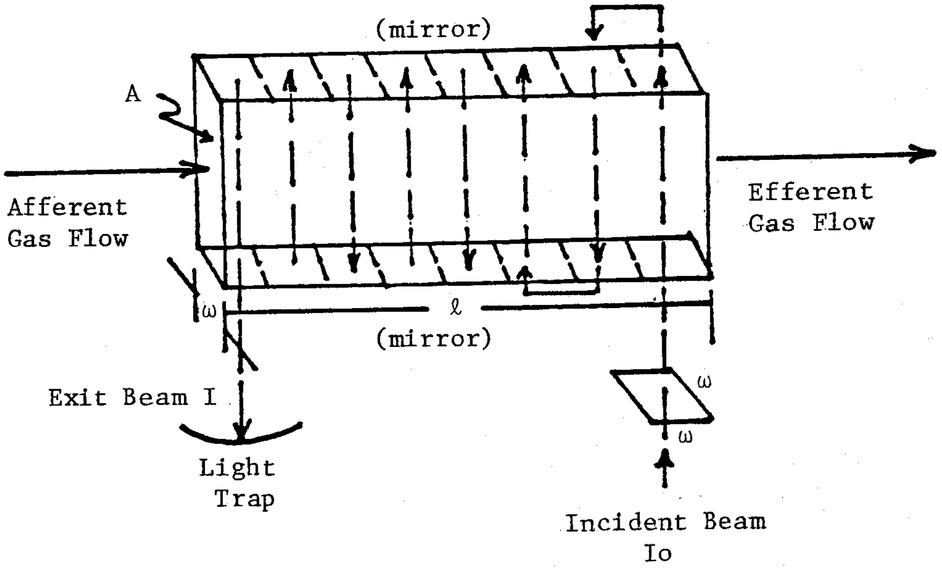

Fig. 5.3 -- Idealized Reaction Chamber
(For ease of visualization, the light beam is shown with rectangular cross-section. The several traverses of the light beam fill the chamber's volume.)

passes through a columnar section of the chamber of height A/ω and area equal to the cross-sectional area of the beam $A_b = \omega^2$.

Given this model, we may now write the appropriate design equations. The first is

$$I_e = I_0 - \beta h\nu\rho b/t_p \qquad \text{(absorption law)} \qquad (5.22)$$

where I_0 is the incident intensity (photon flux) and I_e is the pulse-averaged exit intensity. β is the number of photons of energy $h\nu$ required per molecule for dissociation, ρ is the number density of the reactant species, b is the total path length, and t_p is the pulse length of the laser. This equation represents the conservation of energy over a pulse time. An absorption law of Beer's form is not appropriate at the high intensities considered here because the absorption cross-section is not linear but rather a highly non-linear function of the fluence.

The next equation defines the total path length b as

$$b = \frac{A}{\omega}\left(\frac{\ell}{\omega}\right) \qquad \text{(path length)} \qquad (5.23)$$

where A/ω is the length of a single traverse across the reaction chamber and $\ell/\omega(=\ell\omega/\omega^2)$ is the number of traverses. The velocity of gas flow through the chamber is

$$v = \frac{q}{A} \qquad (5.24)$$

where q is the volume flow rate. This flow, corrected for pressure drop, is crudely determined as that necessary to achieve the maximum allowable solvent concentration (TLV) in a degreaser assuming a (known) constant evaporation rate (S) and complete mixing of solvent vapor and incoming air. Mathematically, the mass balance over such a degreaser is

$$0 = \dot{S} - q \left(\frac{P_c}{P}\right) \rho_d = \dot{S} - q\rho \qquad (5.25)$$

where ρ_d is the number density in the degreaser, P_c is the low pressure in the reaction chamber, and P is ambient pressure.

The conditions on the laser are the total energy delivered to the cell per pulse,

$$E = I_0 A_b t_p \quad \text{(energy per pulse)} \qquad (5.26)$$

and the chemical decomposition requirement (e.g., Keefer et al., 1976; Lussier and Steinfeld, 1977; Lyman et al., 1981) that the fluence at the beam exit point be (at least) equal to a compound specific threshold value (T), i.e.,

$$I_e t_p = T \quad \text{(threshold condition)} \qquad (5.27)$$

The final condition derives from the requirement that the gas flow be slow enough to not allow any gas to escape the photon beam between pulses. Mathematically, this is formulated so that the time for the gas to pass through the cell (ℓ/v) equals or exceeds the time between pulses, i.e.,

$$\frac{\ell}{v} \geq \frac{1}{H} \quad \text{or} \quad H \geq \frac{v}{\ell} \tag{5.28}$$

where H is the pulse repeat frequency.

With b, ℓ, $A_b(=\omega^2)$, S, T, ρ, β, t_p, and ν specified as physically reasonable input parameters, Eqs. (5.22) to (5.28) may be solved for I_e, I_0, A, q, v, EH, and H. EH (the average power output) and H specify the laser required. q (and the cell pressure) specify the pump required.

The solution for EH and H is obtained by substituting Eqs. (5.26) and (5.27) into (5.22) to give

$$E = A_b\ (T + \beta h\nu\rho b) \tag{5.29}$$

Solving Eqs. (5.23), (5.24), and (5.25) simultaneously for v, followed by substitution into Eq.(5.27) yields

$$EH \geq \frac{A_b \dot{S}}{\rho b \omega^2} (T + \beta h \nu \rho b) \tag{5.30}$$

or

$$H \geq \frac{\dot{S}}{\rho b \omega^2} \tag{5.31}$$

To keep the average power demand of the laser to a minimum, Eq. (5.31) indicates that the largest possible path length b be employed. Note also that, since $A_b = \omega^2$, Eq. (5.30) indicates that the average power requirement does not depend on the cross-sectional area of the beam; however, as indicated by Eq. (5.31) the pulse rate does.

We have evaluated Eqs. (5.29), (5.30), and (5.32) and solved for all other variables using the parameters in Table 5.1. The variables are shown in Table 5.2. Because of their ready availability, the spectroscopic parameters ($h\nu$, β, T, P_c, t_p) are based on experimental values appropriate to CFC-22 (Grunwald and Olszyna, 1976); the evaporative loss parameter (S) is based on the amount of (CFC-113) solvent evaporating from an average-sized 120ℓ degreaser (Palmer et al., 1980); the beam diameter is based on a large readily available size; and the reaction cell parameters (b and ℓ) are based on our judgment of the longest pathlength attainable within reasonable dimensions and with available optics.

Table 5.1

PARAMETER VALUES

Parameter	Value	Description
S	.002 moles/sec	mass loss per day of CFC-113 from an average-sized degreaser (Palmer et al., 1980)
ρ	2.41×10^{15}/cc	0.1 of the CFC TLV (1000 ppm) (ACGIH, 1981)
$h\nu$	2.15×10^{13} erg	photon energy corresponding to $\nu = 1082\ \text{cm}^{-1}$
β	23 photons/molecule	number of photons to dissociate CFC-22 at 50 torr (Grunwald and Olszyna, 1976)
T	12j/cm^2	fluence for high reaction probability in SF_6 system; consistent with upper bound required for CFC-22 (Lyman et al., 1981; Sudbo et al., 1978b)
t_p	50 nsec	pulse length; selected low enough to prevent collisional loss of energy (Grunwald and Olszyna, 1976)
A_b	1 cm^2	typically available, large sized beam cross-section (Laser Focus, 1979)
ℓ	60 cm	reaction chamber length, arbitrarily convenient
b	3600 cm	largest easily attained path length (our judgment)

Table 5.2

NUMERICAL VALUES OF VARIABLES

Variable	Value	Description
q	5×10^5 cc/sec ($1059\ ft^3$/min)	volume flow in chamber (at 0.1 atm)
v	8.3×10^3 cm/sec	face velocity in chamber
A	$60\ cm^2$	cross-sectional area of flow
I	$2.4 \times 10^8\ watts/cm^2$	pulse-averaged exit intensity
I_0	$3.3 \times 10^8\ watts/cm^2$	incident intensity
H	≥ 139/sec	pulse repeat rate
EH	≥ 2260 watts	average laser output power
E	16.3j	pulse energy

The Example System Attainability and Cost

According to the values of Table 5.2, the average power requirement of the laser in our simple example is 2260 watts with a repeat rate of 139 pulses/sec or greater. These values, together with the assumed pulse length of 50 nsec and 1 cm^2 beam cross-sectional area, completely define the laser. Such criteria can be met by currently available lasers, such as the LASAG Model LIMOCOL50EQ at $45K (Laser Focus, 1979) with a maximum output of 10^4 watts. (Note that this is actually oversized by a factor of 4 relative to our calculated requirement (Table 5.2). Based on our flow rate, q, of 1059 ft^3/min (Table 5.2) and plant design tables (Peters and Timmerhaus, 1968), our assumed operating pressure of 0.1 atm can be met by a rotary pump and 35 hp motor. The cost of the pump system is about $60K but will be lower if the working pressure can be raised. (If steam is available in a plant, a steam injection method should also be able to lower this cost.) Thus, according to these rough estimates, the capital cost of a crude system capable of destroying 56 moles of solvent per day at a concentration of 1000 ppm is on the order of $100K. For comparison, a carbon adsorption system plus steam source that can handle the same solvent loss appears to fall into a similar price range.

Such estimates are only suggestive, however, and are presented only to show that technical and cost feasibility may be within reach. *Further research should address this feasibility question in detail, resolving the significant uncertainties that still remain in quantifying the decomposition physics, and optimizing the reactor itself.* The deficiencies in the optimization of the simple reactor discussed above, in fact, provide a menu for future research. First, for example, most of the incident laser beam energy (72 percent) is still present in the exit beam and thus the possibility of rerouting it should be examined so that the laser is only required to make up the energy difference on the second pass. Second, only 22 percent of the maximum laser output is being utilized in our example. Therefore, it is important to examine if this excess power can be traded for an operating pressure closer to 1.0 atm; this power might be used to make up the additional energy being transferred to the buffer gas at high pressure. If this proved feasible, then the pump requirements might be significantly reduced or eliminated. Third, there will be loss of reflectivity of the mirror due to surface deposition. It is important to assess the source and magnitude of this loss in various applications. Methods for minimizing the loss can then be examined.

COMPARISON WITH ALTERNATIVE SYSTEMS

To assess the practicality of employing our proposed laser system, its costs should be compared to those of alternative systems that perform a similar function. The theoretical and experimental work described in this Note must be done before the laser system can be fully characterized; an estimate of the operating costs and a better estimate of the capital cost would then be possible. For current purposes, we will use the preliminary system cost estimate of $100K given in the last subsection. We will compare this with the capital costs of two systems, catalytic oxidation and carbon adsorption, that are currently used to treat chlorinated gas streams.

Costs of the catalytic oxidation of chlorocarbons are presented in EPA (1980b). Although the low flow rates (100 cfm) that are present in our example industrial setting are not considered in the EPA publication, extrapolation to this lower rate should be reasonable. It appears from Figs. IV-1 and IV-2 of the EPA document that the installed capital costs of catalytic oxidizer systems (excluding scrubbers) operating at 100 cfm lie in the range of $150K to $200K. This exceeds the preliminary capital cost estimate of the proposed laser system.

Carbon adsorption systems are commonly used to capture chlorocarbon solvent vapor emissions. Desorption is usually accomplished with steam. The carbon system and steam source together have a capital cost on the order of $100K (private communication with Vic Manufacturing Company). Carbon adsorption is apparently not used routinely by trichloroethylene and methyl chloroform users, because of reformulation problems. Trichloroethylene and methyl chloroform require stabilizer additives which are water soluble. These stabilizers are lost in the desorption step and reformulation is required before the solvent can be reused. Although carbon adsorption systems should be extremely efficient, they rarely are in practice. One source (OAQPS) reports that a test performed using a carbon adsorption device on an open top vapor degreaser resulted in a 60 percent emissions reduction. Two other systems that were tested achieved a 21 and 25 percent emissions reduction; in a fourth system, carbon adsorption was found to increase emissions by 8 percent. Inefficient adsorption devices can therefore lower emissions but may not prevent them altogether.

For further work, two sources (Vic Manufacturing Co. and EPA, 1980b) could be used to derive better estimates of the total costs and efficiencies of carbon adsorption and catalytic oxidation systems. These data, together with the more detailed theoretical and experimental investigations, could provide a refined estimate of the comparative costs of the laser system.

VI. FUTURE WORK

We have identified one area of future research involving a two-laser system that is worthwhile to pursue. Such a system, composed of an ultraviolet and an IR laser, may offer certain advantages for the decomposition of hazardous chlorinated gases. Further work in this area would be useful.

Ultraviolet techniques alone are not especially appropriate for decomposition in an air-containing gas phase. The chlorinated methanes and the ethylenes have intense absorption in the vacuum ultraviolet region (Haak and Stuhl, 1979; Berry, 1974) where both atmospheric oxygen and ozone also have strong absorptions. Upon irradiation of the chlorinated gases, oxygen would absorb most of the radiation. Consequently, to use ultraviolet radiation to decompose the gases, an evacuated chamber would be required. This would be impractical in an industrial setting and extremely expensive as well.

Future work could examine the feasibility of using a combination of ultraviolet and infrared irradiation for dissociating chlorinated species in the gas phase. In such a system, although two lasers would be required, evacuation would not be necessary. The vacuum ultraviolet region extends from 2000 A and below. The ultraviolet region, where oxygen absorption does not interfere, extends from 2000 A to 4000 A. VC, VDC, and TCE have a very strong absorption band between about 1900 A and 2000 A. Thus, if about 100 A (2700 cm^{-1}) in energy could be supplied initially by an infrared laser, the ultraviolet region would be accessible. In effect, the infrared laser would be used to supply the energy necessary to "transfer" the irradiation frequency from the vacuum ultraviolet to the near ultraviolet region. Tunable infrared lasers operating in the 3.3 μm range are available (Hai-Lung Dai et al., 1979). This method, the use of two lasers for gas phase decomposition, appears to offer some promise; it is a fruitful area for future investigation.

VII. CONCLUSIONS

The preliminary analysis presented in this Note is based on existing laboratory decompositions and a hypothetical reactor design. These data suggest that laser destruction of hazardous chlorine-containing gases is promising. Nevertheless, a more complete investigation of the physics of these systems would be required to establish the feasibility of the method.

The additional research would involve modifying and implementing the existing Lyman and STG models. These models would be tested initially for their ability to accurately portray the multiphoton decomposition characteristics of vinyl chloride, a molecule that has been widely studied experimentally. Concurrent laboratory experiments of vinylidene chloride and trichloroethylene could be conducted to provide data on the influence of inert and oxygen-containing buffers and product yields as a function of gas pressure, laser frequency, and fluence. The results of these experiments could be used to parameterize the multiphoton dissociation models.

A new model, based on the Lyman and STG models, could be developed to describe the two-step dissociation characteristics of ethylene dichloride and methyl chloroform. The second step in the dissociations, the decomposition of vinyl chloride and vinylidene chloride, would already be characterized by the original Lyman and STG models. This description would require modification to account for the vibrational excitation of vinyl chloride and vinylidene chloride as they emerge from the first-step decomposition. Experimental data on the first-step decomposition of ethylene dichloride and methyl chloroform could be used to augment the existing models.

The final task would be to couple the description of the dissociation of the molecules with a model for a photochemical reactor. This would allow a selection of a preliminary reactor geometry, development of the design equations, and estimation of the laser and pressure requirements for various flow rates.

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