

Lawrence Berkeley National Laboratory

Recent Work

Title

Applications of Matrix Infrared Spectroscopy to Mapping of Biomolecular Reaction Paths

Permalink

<https://escholarship.org/uc/item/8zq5n0v1>

Author

Frei, H.

Publication Date

1992



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

CHEMICAL BIODYNAMICS DIVISION

To be published as a chapter in *Vibrational Spectra and Structure*,
J.R. Durig, Ed., Elsevier Science Publishers, The Netherlands, 1992

Applications of Matrix Infrared Spectroscopy to Mapping of Biomolecular Reaction Paths

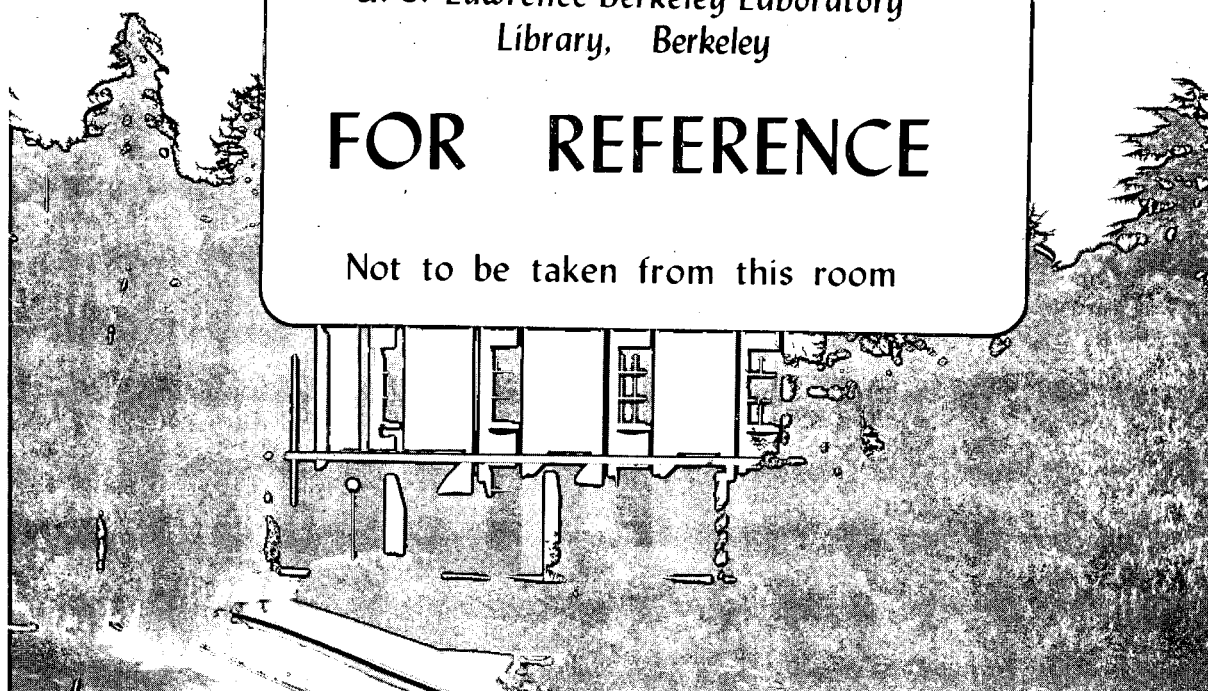
H. Frei

November 1991

U. C. Lawrence Berkeley Laboratory
Library, Berkeley

FOR REFERENCE

Not to be taken from this room



DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Applications of Matrix Infrared Spectroscopy to Mapping of Biomolecular Reaction Paths

Heinz Frei

Chemical Biodynamics Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

November 1991

This report has been reproduced directly from the best available copy.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

APPLICATIONS OF MATRIX INFRARED SPECTROSCOPY TO MAPPING OF
BIMOLECULAR REACTION PATHS

Heinz Frei

Chemical Biodynamics Division, Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

I.	INTRODUCTION	1
II.	OXYGEN TRANSFER REACTIONS.	4
	A. Photooxidation of Hydrocarbons by Nitrogen Dioxide	
	B. Ozone as Oxygen Donor	
	C. Photochemistry of Molecular Oxygen	
III.	HYDROGEN TRANSFER REACTIONS.	42
IV.	CONCLUDING REMARKS.	46
	ACKNOWLEDGEMENTS.	48
	REFERENCES.	49

I. INTRODUCTION

Trapping of chemical intermediates upon photo-initiation of bimolecular reactions in solid inert gas matrices is an established method for elucidation of reaction paths. At the heart of the success of this method lies the fact that radicals, sometimes even biradicals, and many closed shell species that are too unstable for observation at ambient temperature can be stabilized indefinitely in the cryogenic environment. Furthermore, infrared spectroscopy, a readily available, powerful diagnostic tool can be employed for determination of the structure of even rather complex polyatomic intermediates. Since the development of the matrix isolation technique by Pimentel in the 1950's [1] the goal of most of the numerous photochemical studies that have been conducted in inert solid matrices has been the generation of new chemical species. However, the structure of the latter reveals, in many cases, details about the mechanism of the synthetic pathway itself. Many interesting examples of such bimolecular reactions in matrices, typically initiated by photodissociation of a reactant with UV radiation from a mercury arc source, are discussed in conjunction with related topics in recent reviews by Perutz [2-4], Jacox [5], Dunkin [6], Hauge et al. [7], and Almond and Downs [8].

The availability of intense monochromatic light from tunable lasers has allowed matrix photochemists to focus on aspects of mechanism and dynamics of bimolecular reactions that go well beyond what can be learned from experiments with conventional broad band sources. There are several reasons for this. Reactions on multiple energy surfaces, often difficult to separate even under the best circumstances, are minimized or altogether avoided. In favorable situations, reaction surfaces can be selectively accessed through an appropriate choice of the photolysis wavelength. Photon excitation energies can be adjusted to ensure that reaction intermediates emerge with the least amount of excess internal energy. This improves the chances for stabilization of transients by the cold matrix environment prior to rearrangement, fragmentation, or other undesired continued chemistry. Such intermediates, if trapped in their nascent structure, reveal

intimate details of the reaction mechanism and energy path. Of course, new unstable species so obtained may become of interest in their own right. Measurement of the growth kinetics of infrared product absorptions as a function of the photolysis wavelength allows one to determine the photon energy dependence of reaction quantum efficiencies and product branchings, furnishing clues about the electronic surface(s) involved in the reaction and in some cases even about the dynamics of transients. Moreover, control of the photolysis photon energy minimizes the possibility of loss of trapped transients due to secondary photolysis, a mundane but rather frequent problem.

Early photochemical work with infrared lasers brought to light a few examples of vibrationally induced bimolecular reactions in cryogenic solids [9-11]. In recent years, a growing number of reports have appeared on bimolecular chemistry in matrices initiated by selective electronic, even single vibronic, excitation of reactants by wavelength controlled UV, visible, or near infrared light. This work revealed unprecedented insight into regiochemistry, stereochemistry, and electronic states of transients accessed along the reaction path. The objective of these studies falls most often in one, or both, of two categories. One is elucidation of the mechanism of a gas or solution phase reaction that currently cannot be gained by time resolved in-situ monitoring in the mobile phase. This includes reactions of importance for chemical synthesis, or of interest in specific areas like combustion or atmospheric chemistry. Despite the enormous advances in time-resolved optical spectroscopy in recent years, particularly in infrared [12] and Raman spectroscopy [13], transients of many familiar gas and solution phase reactions are still eluding detection by these for structure determination crucial techniques. This hinges mainly on the difficulty of obtaining complete infrared spectra of complex polyatomics with lifetimes in the 10^{-10} - 10^{-13} sec. range (which is typical, for example, for biradicals), and of obtaining Raman spectra of short lived transients that do not have chromophores suitable for resonance enhancement. Considerable new insight into mechanism and dynamics of fluid phase reactions can be gained from a study of the reactions in a matrix provided that energy surfaces accessed in the

matrix reaction can be identified e.g. by aid of photolysis wavelength dependence studies, and effects on the continued chemistry imposed by the solid matrix cage are properly taken into account. A second objective of studying bimolecular reaction paths in rare gas solids is to explore how the special situation of photo-induced chemistry of cage pairs can be exploited for product specific synthesis of high valued compounds. One such special aspect, already referred to above, is product control by access to low energy paths that generate primary photoproducts with minimal excess internal energy, thereby reducing the likelihood of subsequent rearrangement or fragmentation. Low energy paths of bimolecular systems lie typically below dissociation limits of reactants and can therefore be accessed, in principle, from bound, non-predissociative reactant levels. A solid matrix is a natural environment for bimolecular photochemistry initiated by excitation below dissociation thresholds since reactant nearest neighbors enclosed in a matrix cage are held in contact indefinitely, hence absorption of a photon occurs always while the partners are in a state of collision. Irradiation during a collision is the best way to initiate chemistry from bound levels as the reaction can only occur if excitation is sustained through the moment of collision. Although use of room temperature solid matrices may be the ultimate goal in many cases (for example hydrocarbon polymers or zeolites, where some success in terms of product control has already been accomplished [14]), work in cryogenic matrices is a good starting point because it permits us to fully exploit the diagnostic advantages of infrared spectroscopy in rare gas solids for determination of the factors that favor product control.

In this article we will survey recent progress in elucidation of photo-initiated reactions of collisional pairs and weak complexes in cryogenic matrices. Discussion will concentrate on oxygen and hydrogen transfer reactions since the most significant advances have been made in these particular areas. Emphasis is on examples that illustrate how structural information on trapped transients can be used to derive new regio- and stereochemical details of bimolecular reaction paths, and how determination of the photolysis wavelength dependence of reaction quantum efficiencies and product branchings can be employed to uncover energy paths. Dynamical

aspects unique to the photochemistry of collisional pairs and weak complexes will be discussed, and frequent reference to results from studies in solution, gas phase, and molecular beams will be made. Progress in the understanding of photochemical reactions involving transition metal complexes or metal atoms, most recently reviewed by Perutz [2] and by Almond and Downs [8], will not be discussed here. Since many experimental aspects of photochemical work in cryogenic matrices have been dealt with in two monographs [8,15] not long ago, we will expand only on those technical aspects that are unique to the studies reviewed in this article.

II. OXYGEN TRANSFER REACTIONS

Several research groups have focussed over the past few years considerable effort on photooxidation of organic and inorganic molecules by nitrogen dioxide, ozone, and molecular oxygen in cryogenic matrices, which has led to fascinating new insight into this reaction type. Aside from its importance for combustion [16] and atmospheric chemistry [17], understanding of the mechanism and dynamics of O transfer reactions is crucial for product specific synthesis in general, and for progress in controlled oxidation of abundant hydrocarbons to organic building blocks in particular [18,19]. In fact, product specific, in particular stereospecific, oxidation of small unfunctionalized hydrocarbons is currently a central topic in catalysis research. The first areas reviewed in this section, mild photooxidation of small alkenes and alkynes by NO_2 , relates directly to this problem.

A. Photooxidation of Hydrocarbons by Nitrogen Dioxide

In a search for product specific oxidation of small unfunctionalized alkenes and alkynes we have explored over the past several years low energy oxygen transfer paths of NO_2 •hydrocarbon pairs in solid rare gas matrices. NO_2 is an ideal O atom donor because it absorbs throughout the UV, visible, and a large part of the near infrared spectral regions, hence excitation by light over a wide range of wavelengths can be used to search for and elucidate controlled hydrocarbon oxidation paths. Scheme I shows products and photolysis thresholds of several reactions that we have studied in detail. As the products indicate, these photooxidations are indeed tightly controlled. For example, epoxides are exclusive products of olefin oxidations except when the $\text{C}=\text{C}$ group is in the terminal position. In the latter case, aldehydes may also be formed. A high degree of diastereospecificity is observed in the case of epoxidation of cis and trans-2-butene. Ketenes are the sole products in the case of alkyne oxidation, which demonstrates especially the mild nature of these reactions. In no instance were products observed that would result from break-up of the carbon skeleton. It is important to note that this product specificity is primarily a consequence of access of specific reaction surfaces rather than the low temperature of the cryogenic environment, as will become clear from the examples presented in this section.

A unique aspect of these photo-initiated oxygen transfer reactions of matrix isolated NO_2 •hydrocarbon pairs was concurrent trapping of monoradicals, namely alkyl nitrite radicals in the case of alkene and allene oxidation, and iminoxy radicals in the case of O atom transfer to acetylenes. Elucidation of the origin of these species became the key to the reaction paths. Two observations revealed that in each case the radical is a NO trapped biradical, formed upon oxygen transfer to the CC multiple bond, that acts as a common precursor of the final oxidation product and the nitrite (or iminoxy) radical. First, the branching ratio of the trapped radical and final oxidation product could be manipulated by CH_3 group and even by D isotope substitution.

Second, regio- and/or stereochemistry of the carbon frame of the trapped radical and oxidation product was found to be correlated. Both points will be illustrated by the reactions discussed below. Study of the infrared spectra of these trapped radicals and their photodissociation chemistry allowed us to infer the nascent structure (including conformation), in some cases even the nascent electronic state of these transient biradicals. Several examples will be presented here, each revealing a new detail about hydrocarbon oxidation paths.

1. Photooxidation of Acyclic Alkenes

a. 2-Butene + NO₂. Epoxidation of trans - and cis-2-butene by photolysis of 2-butene•NO₂ pairs gave us an opportunity to explore the question of stereochemical control upon O transfer to a CC double bond[20-22]. Alkene•NO₂ collisional pairs were prepared in solid matrices by co-depositing gaseous alkene/Ar and NO₂/Ar mixtures through separate vacuum lines onto a 12K cooled, infrared transparent CsI salt window. Concentrations were chosen so that typically 10-20% of the alkene molecules would have a NO₂ nearest neighbor. Infrared spectra were recorded after preparation of the matrix and following each period of irradiation of the matrix with monochromatic light from a continuous wave (cw) Ar ion laser (8 discrete emission lines in the 458-515 nm region), or from an Ar or Kr ion laser pumped cw dye laser (continuously tunable from 520-1000 nm). Neither infrared nor visible/near infrared spectra revealed any special features of alkene•NO₂ cage pairs that would indicate formation of a complex, hence our designation "collisional pairs".

Infrared spectra obtained upon irradiation of trans-2-butene•NO₂ pairs with visible light revealed trans-2,3-epoxybutane as exclusive oxidation product (under concurrent generation of NO). Fig. 1a shows a difference spectrum of the region 2000-400 cm⁻¹ after 60 min. irradiation of a matrix trans-2-butene/NO₂/Ar=2.5/1/200 at 610 nm. No cis diastereomer of the epoxide was

observed. Diastereomer identification was unambiguous as infrared matrix spectra of both *cis*- and *trans*-2,3-epoxybutane have been reported in the literature [23]. Comparison of absorbance growth of the relatively intense 1118 cm^{-1} *trans*-epoxide band with the absorbance detection limit at 1102 cm^{-1} (where a *cis*-epoxide band with similar extinction would absorb) allowed us to put a lower limit of 50 on the *trans* to *cis*-2-butene oxide product branching ratio. Apart from the spectra of epoxide and NO, a set of five additional infrared product bands appeared that could not be assigned to any known species. The most prominent bands, which are readily discerned from spectrum (a) of Fig. 1, are at 1646 and 755 cm^{-1} (labelled I_t). Frequencies of all five new absorptions including those observed upon reaction of *trans*-2-butene with $\text{N}^{16}\text{O}^{18}\text{O}$ and N^{18}O_2 are presented in the top section of Table 1. Similarly, photolysis of *cis*-2-butene• NO_2 pairs with visible light gave a new species I_c concurrently with *cis*-2,3-epoxybutane and NO (complete diastereospecificity only at high matrix dilution, see below). The spectrum of I_c is given in the bottom section of Table 1. Although infrared frequencies of I_c are close to those of I_t as can be seen from Table 1, the spectra of the two species are distinctly different. Fig. 2 shows a pair of closely spaced product bands I in the $800\text{--}700\text{ cm}^{-1}$ region, namely the 755 cm^{-1} absorption of I_t observed upon 590 nm photolysis of *trans*-2-butene• NO_2 pairs (Fig. 2a), and the 772 cm^{-1} absorption of I_c produced in a corresponding *cis*-2-butene + NO_2 experiment (Fig. 2b).

Clues to structure and origin of the two trapped species I came from the spectra of Table 1, from photodissociation behavior, and from thermal interconversion experiments. Photodissociation of I_t occurred at all wavelengths shorter than 610 nm . The dissociation chemistry is most readily monitored by brief irradiation of I_t with green (514 nm) light after accumulation of the species by prolonged photolysis of *trans*-butene• NO_2 pairs with red light. The resulting infrared difference spectrum, Fig. 1b, shows that I_t photodissociates to *trans*-2,3-epoxybutane and NO. This implies that I_t has the composition $\text{C}_4\text{H}_8\text{O}_2\text{N}$. I_c was found to photodissociate to methyl propanal and NO (threshold wavelength of 573 nm), hence it is a $\text{C}_4\text{H}_8\text{O}_2\text{N}$ species as well. In fact, warm-up of a matrix containing I_c from 12 to 22 K led to

complete interconversion of I_c to I_t . This is illustrated by the behavior of the 772 cm^{-1} and the 755 cm^{-1} bands shown in Figs. 2c and 2d. Because annealing of the matrix also caused thermal isomerization of N_xO_y species which complicates the spectral region $800\text{--}700\text{ cm}^{-1}$, the effect of matrix warm-up is shown in Figs. 2c and 2d by a comparison of corresponding photo-depletion spectra. Evidently I_c and I_t are stereoisomers, I_c being the less stable of the two.

Frequencies and ^{18}O isotope shifts of the intense 1646 cm^{-1} (I_t) and 1652 cm^{-1} (I_c) bands are characteristic for a $\nu(\text{N}=\text{O})$ absorption of a nitrite functional group, while absorptions at 755 cm^{-1} (I_t) and 772 cm^{-1} (I_c) are typical for the N-O stretching mode of a $-\text{O}-\text{N}=\text{O}$ group [24]. In fact, these bands are very close to corresponding absorptions of closed shell nitrite molecules with s-trans conformation about the N-O bond (for example, trans-t-butyl nitrite isolated in solid Ar absorbs at 1638 cm^{-1} [25]. Cis (N-O) forms of closed-shell nitrites have a $\nu(\text{N}=\text{O})$ absorption at substantially lower frequency, in the range $1625\text{--}1605\text{ cm}^{-1}$ [24,26]). Strong support for the $-\text{O}-\text{N}=\text{O}$ group assignment is furnished by frequency shifts of ^{18}O monosubstituted I_t . The shifts of the 1646 cm^{-1} $\nu(\text{N}=\text{O})$ band of 40.5 and 1.3 cm^{-1} (Table 1) are identical with those reported for $\nu(\text{N}=\text{O})$ of ^{18}O monolabelled trans- $\text{CH}_3\text{-O-N}=\text{O}$ [27]. The four-fold splitting of the 920 cm^{-1} absorption of I_t observed upon reaction of trans-2-butene with partially ^{18}O labelled NO_2 ($\text{N}^{16}\text{O}_2/\text{N}^{16}\text{O}^{18}\text{O}/\text{N}^{18}\text{O}_2 = 2/3/1$) confirmed that the species has two inequivalent oxygens (Fig. 3) (equivalent oxygens would give rise to only three bands). The size of the shifts (14 cm^{-1} for $\text{C}_4\text{H}_8^{18}\text{ON}^{16}\text{O}$, 19 cm^{-1} for $\text{C}_4\text{H}_8^{18}\text{ON}^{18}\text{O}$) suggests that this mode contains a strong $\nu(\text{C}-\text{O})$ contribution.

The only species with the formula $\text{C}_4\text{H}_8\text{O}_2\text{N}$ with a nitrite functional group that can conceivably be formed by reaction of $\text{CH}_3\text{-CH}=\text{CH-CH}_3$ with NO_2 is $\text{CH}_3\text{-}\dot{\text{C}}\text{H-CH}(\text{CH}_3)\text{-ONO}$. The fact that the stretching modes of the $-\text{O}-\text{N}=\text{O}$ group of this radical are very close to those of the corresponding (closed-shell) molecule suggests that in its ground state the nitrite group is only weakly perturbed by the unpaired carbon electron. The low barrier to interconversion of I_c to I_t as

indicated by the matrix warm-up experiment (Figs. 2c and d), further suggests that the structural difference between the two forms lies in the conformation about the central CC bond (thermal isomerizations that proceed at 22K on a timescale of minutes have barriers not higher than about one kcal mol⁻¹ [28]). The fact that I_c is less stable than I_t would be consistent with I_c having a synclinal arrangement of the methyl groups, while I_t would have a more stable anticlinal conformation with respect to the CH₃ groups. This is supported by infrared spectroscopic evidence. As can be seen for Table 1, species I_c has four fundamental absorptions between 2000 and 600 cm⁻¹ that can be associated with vibrations of the butyl fragment (1374, 1052, 837, and 651 cm⁻¹), while for I_t there are only two (1367 and 1035 cm⁻¹). This is consistent with I_t having a butyl moiety with a conformation close to the centrosymmetric trans form. In this case, half of the bands associated with vibrations of the C₄ fragment are expected to be very weak because of g symmetry with respect to the local inversion center. The syn form lacks such a pseudo-center of symmetry, hence the cross section of most skeletal infrared absorptions would not be subject to such symmetry restriction. Therefore, both spectroscopic evidence and thermal behavior suggest that I_c and I_t differ in their conformation around the central C-C bond, and that I_c has syn and I_t anti conformation with respect to the methyl groups. As can be seen from the Newman projections displayed in Table 1, this conformational assignment may also explain the conformer-specific photodissociation of the nitrite radicals. The oxirane biradical produced upon elimination of NO from I_t has the carbon lone electron p-orbital aligned with the singly occupied p-orbital on the oxygen. This is an ideal geometry for ring closure to occur, and photodissociation of I_t gives indeed exclusively trans-2,3-epoxybutane. By contrast, the CH₃- $\dot{\text{C}}\text{H}$ -CH(CH₃)- $\dot{\text{O}}$ biradical conformer produced upon photo-expulsion of NO from conformer I_c has the lone carbon p-orbital aligned with the CH₃ group on the vicinal carbon, hence in this case stereochemistry is expected to favor CH₃ group migration to give methylpropanal (CH₃-CH(CH₃)-CH=O), as observed. Therefore, the photodissociation, thermal interconversion, and infrared spectroscopic results all indicate that the butyl nitrite radical conformer observed in each case is the one expected if stereochemistry about the former CC double bond is retained.

The most interesting aspect of the nitrite radical is that it shares a transient precursor with the epoxide product and hence furnishes insight into the oxygen transfer mechanism. The first evidence that the paths leading to the two products have a common step was established by observation of a correlation of the stereochemistry of the butyl nitrite radical and epoxide under conditions where partial stereochemical scrambling did occur. This was detected in the cis-2-butene + NO₂ case at high reactant concentration where some trans-butyl nitrite radical and trans-epoxide appeared alongside with the cis products [21] (scrambling never occurred in the trans-butene + NO₂ reaction, under any conditions). The cis/trans product ratio was found to vary with reactant concentration, yet the stereochemical branching of epoxide and nitrite radical was always identical [21]. For example, cis-epoxide/trans-epoxide and I_c/I_t ratio changed both from 6 to 1 upon increase of the matrix concentration cis-butene/NO₂/Ar from 2.5/1/400 to 2.5/1/100. This correlation between the stereochemistry of the two products implies a common transient precursor whose conformation dictates the stereochemistry of both nitrite radical and epoxide. The sole precursor which is consistent with the high degree of stereochemical retention and the photolysis wavelength dependence of the reaction quantum efficiency is an oxirane biradical CH₃- $\dot{\text{C}}\text{H}$ -CH(CH₃)- $\dot{\text{O}}$, shown in Scheme II. This means that excitation of 2-butene-NO₂ pairs results in direct oxygen transfer to the CC double bond. The oxirane biradical so formed is stabilized by two processes that compete on a fast (presumably psec) timescale, namely ring closure to form epoxide on the one hand, and, on the other, radical combination with NO cage coproduct to give butyl nitrite radical. The interesting point is that the transient biradical is trapped in its nascent conformation as indicated by the high degree of retention even in the case of unstable biradical conformers (cis-2-butene oxirane biradical). This means that by determining the conformation of the spectroscopically observed nitrite radical we are able to probe for the first time the structure of the transient biradical that controls the stereochemical outcome of the oxidation. Moreover, the fact that epoxide is preceded by an oxirane biradical implies that oxygen transfer is asymmetrical, resulting in sequential formation of the two C-O bonds rather than direct generation of epoxide in a

single step through O atom insertion into the C=C bond. This touches upon a long standing controversy between two mechanisms proposed for epoxidation of alkenes by closed shell oxidizers like peroxy acids [29], namely oxygen atom insertion into the CC double bond in a single step [30] and sequential formation of C-O bonds following unsymmetrical attack of the C=C group [31]. Since thermal epoxidation of alkene by closed shell peroxy acid leads to a (spin) singlet primary product similar to long visible wavelength induced oxygen transfer of NO₂-alkene pairs, it is very probable that peroxy acid oxidation involves a singlet oxirane biradical as well. Hence, our NO₂ studies add support to a sequential formation C-O bonds upon thermal alkene epoxidation by closed shell oxidizers.

Kinetic analysis of product absorbance growth at several photolysis wavelengths, analogous to the one performed in the ethylene + NO₂ case explained in more detail in Sect. 1b, showed that the wavelength dependence of the branching between epoxide and nitrite radical can readily be explained in terms of competition between ring closure of the oxirane biradical, which involves a barrier of 1-3 kcal mol⁻¹, and activationless cage-combination with NO. Moreover, the analysis allowed us to determine the extent to which secondary photolysis of butyl nitrite radical contributes to final oxidation product yield at each photolysis wavelength. Visible spectroscopy of alkyl nitrite radicals produced by red photolysis of alkene-NO₂ pairs revealed that photoelimination of NO is caused by absorption of light into a low lying charge transfer state of the radical [32].

b. Ethylene + NO₂. Several ab initio calculations on low lying electronic states of ethylene oxirane biradical CH₂-CH₂-O have recently been reported in the literature [33-36], hence a study of the ethylene +NO₂ reaction allowed us to learn more details about the dynamics of oxygen transfer to an alkene. Products observed upon irradiation of ethylene-NO₂ pairs with visible light were ethylene oxide, acetaldehyde, NO, and ethyl nitrite radical $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-ONO}$ [37]. NO double and single bond stretching modes of the latter were found at 1664 and 773 cm⁻¹, respectively.

These are very close to the corresponding absorptions of (closed shell) trans-ethyl nitrite molecule, indicating that $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-ONO}$ has trans(anti) conformation about the N-O bond. Fig. 4 shows a potential energy diagram based on standard thermodynamic data of reactants and stable products, and on the calculated energy of the $^1\text{D}(\sigma\sigma)$ ground state of $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$. For the latter, agreement exists among the most recent ab initio work by Fueno [34] and Melius [35] (in the $^1\text{D}(\sigma\sigma)$ state, both C and O unpaired p-electron orbitals (first and second greek symbol, respectively) are in the CCO plane (Fig. 4)). As can be seen from the diagram, the observed 574 nm threshold to oxygen transfer of $\text{C}_2\text{H}_4\text{-NO}_2$ pairs lies just above the oxirane biradical ground state, hence reaction induced by yellow light leads most probably directly to the formation of $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ in this ^1D state. Branching between ethylene oxide, acetaldehyde, and ethyl nitrite radical would be dictated by the competition between ring closure of the biradical, 1,2-H shift, and combination with NO cage neighbor. Formation of aldehyde in addition to epoxide is consistent with a very low ab initio barrier for 1,2-H migration of the ^1D biradical state (2-6 kcal mol⁻¹ [34,35]). These competing processes are fast on the timescale of internal rotation of $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ because complete stereochemical retention was observed in the ethyl nitrite radical upon photolysis of cis and trans- CHD=CHD-NO_2 pairs as indicated by mutually exclusive sets of $\dot{\text{C}}\text{HD-CHD-ONO}$ product infrared bands in the fingerprint region (Scheme III). A very short lifetime of the biradical is indeed expected for $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ produced in the $^1\text{D}(\sigma\sigma)$ state because the singly occupied p-orbitals on C and O are perfectly aligned in this state for ring closure, and because the $^1\text{D}(\sigma\sigma)$ biradical state lies on the electronic ground state surface of the epoxide.

An important tool for determining energy paths of these photooxidations is measurement of the product growth kinetics as function of photolysis wavelength. Infrared absorbance growth curves of the three products obtained upon prolonged irradiation of matrices $\text{C}_2\text{H}_4/\text{NO}_2/\text{Ar} = 1/10/100$ at four different wavelengths in the range 574-488 nm are displayed in Fig. 5. As can readily be discerned from the curves, the rate of nitrite radical (I) formation increases steeply with increasing photolysis photon energy, reaching rapidly a plateau at green and blue wavelengths.

Acetaldehyde (A) exhibits a partial induction period at low photolysis photon energies, and ethylene oxide (E) a full induction period at all photon energies. This signals secondary photolysis of accumulated ethyl nitrite radical to C_2H_4O and NO, similar to the photodissociation already encountered in the case of butyl nitrite radical. The differential equations of the corresponding kinetic Scheme IV are

$$d[R]/dt = -(k_1 + k_{3a} + k_{3e}) [R]$$

$$d[I]/dt = k_1[R] - (k_{2e} + k_{2a}) [I]$$

$$d[E]/dt = k_{3e}[R] + k_{2e} [I]$$

$$d[A]/dt = k_{3a}[R] + k_{2a} [I]$$

R represents the reservoir of ethylene- NO_2 pairs. This pool of reactant pairs is depleted by the chemical reaction since ethylene and NO_2 do not undergo diffusion in the 12K rare gas solid. What makes determination of the rate constants k by fitting of the corresponding integrated equations useful is the fact that in the thin optical absorption limit the rate constants are proportional to the quantum yield to reaction, the photolysis laser intensity, and the extinction coefficient of NO_2 [37]. Laser intensity and NO_2 absorption cross section can readily be measured, hence quantum yields to reaction can be calculated. Our experiments are conducted well within the thin optical limit because of the low absorption cross section of NO_2 in the visible ($60\text{--}10\text{ l mol}^{-1}\text{ cm}^{-1}$ in the range between 500 and 600 nm, Fig. 6 [32,38]). We find, for example, that the quantum efficiency to reaction of ethylene- NO_2 pairs $\phi_t = (k_1 + k_{3a} + k_{3e}) / (\epsilon_{vis}^{NO_2} \cdot I_{laser})$ raises very steeply with photon energy above the 574 nm reaction threshold. As shown in Table 2, the increase is over an order of magnitude in the narrow (6 kcal mol⁻¹) energy range between 574 and 514 nm. Such a rapid increase of the reaction quantum efficiency in the vicinity of the barrier to oxirane biradical formation is what one would expect from reaction of vibrationally excited NO_2 if it would behave according to RRK theory.

Indeed, it has been well established by high resolution spectroscopic studies in gas phase and molecular beam that excitation of NO₂ by light at wavelengths longer than the 398nm dissociation threshold to O(³P) + NO results in a highly vibrationally excited molecule with predominant electronic ground state character [39,40]. The reason is that the ²B₂ excited state (which gives NO₂ its oscillator strength in the visible and near-infrared spectral range, Fig. 6) is heavily perturbed by vibrational levels of the ²A₁ ground electronic state. Mixing of ²B₂ and ²A₁ vibronic states is so strong that the photo-excited NO₂ is in effect a highly vibrationally excited species with mostly electronic ground state character. Since a large fraction (two-thirds) of the NO₂ vibrational modes are stretching modes, such high vibrational overtone excitation by visible light (e.g. 16700 cm⁻¹ upon absorption of a 600 nm photon) results in motion of the NO₂-ethylene collisional pair along an asymmetric N-O...C large amplitude stretching coordinate that corresponds approximately to the reaction coordinate for O atom transfer (the O...C=C distance contracts as the N-O bond expands because the C=C group is spacially fixed).

Intermediacy of ethylene oxirane biradical is strongly supported by observation of D isotope effects on product branchings. For example, a kinetic analysis of the C₂D₄ + NO₂ system analogous to that just described for the C₂H₄ + NO₂ case reveals that the branching k_{3e}/k_{3a} between ring closure and 1,2-H shift of transient oxirane biradical increases upon deuteration by at least a factor of 50, namely from ≤ 0.03 for C₂H₄ to 1.7 in the case of C₂D₄ [41]. This large D isotope effect on the H(D) migration path of the biradical is also manifested by the fact that O transfer from NO₂ to cis and trans-CHD=CHD gives exclusively CH₂D-CD=O but no CHD₂-CH=O (as monitored by aldehydic $\nu(\text{C-D})$ (2082 cm⁻¹) and $\nu(\text{C-H})$ (2735 cm⁻¹) absorptions, respectively) [37], which implies that, for $\dot{\text{C}}\text{HD-CHD-}\dot{\text{O}}$, intramolecular D migration cannot compete with H-migration. Interestingly, wavelength dependent photolysis studies of C₂H₄ + NO₂ show that the branching ratio between acetaldehyde and ethyl nitrite radical grows with increasing photon energy (Table 2, column 3). Assuming RRK behavior, this would be consistent

with the proposed competition between stabilization of $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ by 1,2-H shift, involving a small barrier of a few kcal mol⁻¹, and activationless combination with NO cage neighbor. Since reaction is conducted in a 10K environment, this is only possible if the transient biradical reacts while carrying at least several kcal mol⁻¹ excess internal kinetic energy. The implication is that the observed stereochemical integrity upon O transfer to alkene originates from insufficient coupling of stretch and bending modes of the biradical with the torsional degree of freedom and not merely from the low temperature of the matrix environment.

While initiation of ethylene+NO₂ reaction at visible excitation energies up to 22 kcal mol⁻¹ below the NO₂ dissociation limit (398 nm) results in large amplitude O transfer leading to ground state singlet oxirane biradical, photolysis at wavelengths shorter than 398 nm may open up access to triplet $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ chemistry via predissociation of NO₂ to O(³P) + NO, followed by addition of the oxygen atom to the C=C bond. Neglecting spin interaction with the NO coproduct, the conservation of spin rule dictates that the biradical would emerge in a triplet state, most probably the lowest ³D($\sigma\pi$) state of the triplet manifold (Fig. 4) [34,35] (singly occupied p-orbital on C is in the CCO plane, while that on O is perpendicular to the CCO plane). The gas phase chemistry of the triplet biradical has been established by the work of several groups [42-44], most recently by Lee using the crossed molecular beam method [44]. $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ (³D) was found to be subject to two competing processes of about equal importance, namely elimination of H atom to give enolate radical CH₂=CH- $\dot{\text{O}}$, and intersystem crossing to the lower lying $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ (¹D) state. As shown in Fig. 4, the ³D($\sigma\pi$) state of $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ lies 12 kcal mol⁻¹ above the ¹D($\sigma\sigma$) ground state, and ab initio work puts the barrier to H elimination at 18 kcal mol⁻¹, which is 2 kcal below the NO₂ dissociation limit [34,35]. Therefore, CH₂=CH- $\dot{\text{O}}$ + H may be accessible upon thermal reaction of O(³P) with ethylene even in the cryogenic solid. While the products of $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ (¹D) formed by intersystem crossing of $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-}\dot{\text{O}}$ (³D) would be the same as those observed upon direct generation of the ¹D biradical via visible light induced large amplitude O transfer (i.e. acetaldehyde and ethylene oxide), continued reaction of CH₂=CH- $\dot{\text{O}}$ + H may lead to a different

outcome of the chemistry. In fact, photolysis of matrices of composition C_2H_4 (or C_2D_4)/ NO_2 /Ar = 2.5/1/200 with 380 nm laser light led to a new product absorption at 2143 cm^{-1} (2112 cm^{-1}) in addition to spectra readily attributed to acetaldehyde and ethylene oxide [41]. The new band can unambiguously be assigned to the characteristic, intense $\text{C}=\text{C}=\text{O}$ stretching absorption of $\text{CH}_2=\text{C}=\text{O}$ ($\text{CD}_2=\text{C}=\text{O}$). Ketene is indeed an expected product of $\text{CH}_2=\text{CH}-\dot{\text{O}} + \text{H}$ cage chemistry, namely by H abstraction from enolate radical. Formation of acetaldehyde by combination of cage H at the methylene carbon of enolate radical is also possible and probably takes place, but the alternative path, namely combination at oxygen to yield $\text{CH}_2=\text{CH}-\text{OH}$ is not expected to compete with the former because of destructive phase relation of H and $\text{CH}_2=\text{CH}-\dot{\text{O}}$ singly occupied molecular orbitals [45]. In fact, no vinyl alcohol is observed. This conclusion can be considered as definitive since the matrix infrared spectrum of $\text{CH}_2=\text{CH}-\text{OH}$ is known from work by Andrews [46]. Hence ketene is a unique product of triplet oxirane biradical formed along the NO_2 dissociation - $\text{O}(^3\text{P})$ atom addition path, while acetaldehyde and ethylene oxide are exclusive products of $\dot{\text{C}}\text{H}_2-\text{CH}_2-\dot{\text{O}}$ (^1D) formed directly upon visible light induced large amplitude O transfer, as already discussed. This shows that photoexcitation of reactant pairs by tuned radiation allows us to access singlet and triplet reaction paths of the ethylene + NO_2 system selectively, and to monitor the chemistry on each surface separately.

Interestingly, thermal reaction of alkenes in gas phase or solution leads to nitroalkyl radicals, i.e. to C-N bond formation rather than O atom transfer, as shown in Scheme V [47-50]. In the case of reaction of NO_2 with small alkenes in the gas phase Atkinson et al. [47] were able to directly monitor the appearance of alkyl nitro groups by infrared spectroscopy. This difference between matrix and fluid phase alkene + NO_2 chemistry is surprising in view of the fact that NO_2 excited by low energy visible photons is essentially a highly vibrationally excited, electronic ground state species, hence would be expected to exhibit chemistry similar to that of thermally excited $\text{NO}_2(^2\text{A}_1)$. The most likely explanation for the preference of oxygen transfer in the case of alkene- NO_2 pairs in a matrix is furnished by a comparison of the types of reactant nuclear motions

involved in the two possible reaction paths. Namely, in contrast to the asymmetric large amplitude N-O-C stretching motion initiated by preparation of highly vibrationally excited NO₂ in the case of visible light excited NO₂-alkene pairs, the reaction coordinate for electrophilic addition of NO₂ to the C=C group to form a C-N bond is reactant translational motion. In a solid matrix the latter corresponds to a van der Waals motion of the cage partners. The energy of the photoexcited NO₂ is indeed expected to dissipate to the bulk phonon bath via localized lattice vibrational modes, van der Waals modes being among them. The finding that no direct addition of NO₂ to the alkene bond takes place may point to the fact that accumulation of the very large number of quanta in the van der Waals mode that are needed to reach an excitation of 12-15 kcal mol⁻¹ (=E_a of nitroalkyl radical formation) is rendered impossible by efficient transfer of energy to bulk phonon modes. Hence in the case of reaction in the solid matrix O transfer may prevail over electrophilic addition because of the type of nuclear motion that is initiated by reactant photoexcitation: Vibronically excited collisional pairs in a matrix preferentially access a large amplitude oxygen transfer coordinate (E_a ≈ 45 kcal mol⁻¹) while ignoring the lower barrier translational (in the solid: van der Waals) coordinate that would lead to C-N bond formation by NO₂ addition.

c. Isobutene + NO₂. NO trapping of transient oxirane biradicals in their nascent structure gave us an opportunity to explore detailed regio- and stereochemical paths of various olefin oxidations. For example, which side of an unsymmetrically substituted alkene, like isobutene, is attacked upon photooxidation by NO₂? Red light induced photolysis of (CH₃)₂C=CH₂·NO₂ pairs was found to yield a single butyl nitrite radical isomer with infrared absorptions at 1644, 818, and 754 cm⁻¹ [51]. Products generated upon visible light induced photoelimination of NO were isobutene oxide and methylpropanal, identified by comparison of product infrared spectra with those of authentic samples taken from the literature. While the epoxide could be formed, in principle, by secondary photolysis of nitrite radical with structure (CH₃)₂C(ONO)- $\dot{\text{C}}\text{H}_2$ or structure (CH₃)₂ $\dot{\text{C}}\text{H}$ -CH₂-ONO, the aldehyde can only originate from

photodissociation of the isomer with the terminal ONO group. Since only a single nitrite radical isomer is observed, it must have the $(\text{CH}_3)_2\dot{\text{C}}\text{H}-\text{CH}_2-\text{ONO}$ structure. This implies that oxygen transfer is completely regioselective, leading exclusively to oxirane biradical $(\text{CH}_3)_2\dot{\text{C}}-\text{CH}_2-\dot{\text{O}}$ by attack on the terminal carbon (Scheme VI). This biradical isomer has the carbon lone electron on a tertiary C, while O attack on the central carbon would result in a radical center on a primary carbon. Hence, oxidation occurs not only at the sterically less hindered side of the C=C bond, but also gives the thermodynamically more stable oxirane biradical. This is the first time that the precise regiochemistry of O transfer to isobutene has been established.

2. Cycloalkene Epoxidation

Wavelength selective photochemistry of cycloalkene- NO_2 collisional pairs allowed us to address for the first time a subtle stereochemical question posed by ring epoxidation, namely, which side of the C=C bond is attacked by oxygen. We found in the case of cyclohexene- NO_2 pairs in solid Ar that oxygen transfer can be induced at wavelengths as long as 600 nm, and that cyclohexene oxide is the sole final oxidation product (Scheme VII) [52]. While comparison of the (half-chair) structures of reactants and products gives no clue as to the branching between the two possible diastereomeric O transfer paths, infrared spectra of cyclohexyl nitrite radical, if formed, would allow us to tackle this problem. Two distinct sets of nitrite radical infrared absorptions grew in upon photolysis of cyclohexene- NO_2 pairs by red light as indicated by intense doublets in the $\nu(\text{N}=\text{O})$ and $\nu(\text{N}-\text{O})$ regions, displayed in Fig. 7. The spectra of Fig. 7 actually show the depletion of the trapped species by wavelength selective photodissociation at 545 nm (spectrum a) and 514/448 nm (spectrum b) following accumulation of nitrite radical by 590 nm excitation of cyclohexene- NO_2 pairs. Comparison of spectra a and b indicates the preferential depletion of one species ($1644/756\text{ cm}^{-1}$, labelled I_2) over the other ($1655/769\text{ cm}^{-1}$, labelled I_1) upon 545 nm

photolysis. On the basis of these selective photodissociation experiments, all 16 infrared bands of the nitrite radical product (and the heavy isotope analogues) could be separated into these two groups, as shown in Table 3. Secondary photolysis of both I_1 and I_2 gave cyclohexene oxide and NO, which confirmed the identity of the two species as cyclohexyl nitrite radical stereoisomers.

The N=O stretching absorptions of the two cyclohexyl nitrite radical isomers at 1655 and 1644 cm^{-1} are close to the $\nu(\text{N=O})$ bands of alkyl nitrite radicals discussed above, and the N=O stretch of closed-shell cyclohexyl nitrite (1664 cm^{-1}) which is known to have trans conformation about the N-O bond [24]. Therefore, I_1 and I_2 have most probably the same (trans) conformation about the N-O bond, hence isomerism originating from internal rotation of the nitrite group cannot be responsible for observation of two distinct cyclohexyl nitrite spectra. However, ^{18}O frequency shifts indicate that I_1 is a cyclohexyl nitrite radical with an equatorial, I_2 one with an axial C-O bond. As can be seen from observed ^{18}O isotope frequency shifts in the 1200-800 cm^{-1} range given in Table 3, the C-O stretching mode of I_1 absorbs mainly at 1050 cm^{-1} , that of I_2 at 960 cm^{-1} . According to an infrared study of 4-tert-butylcyclohexanol chair conformer the stretching mode of an axial C-O bond absorbs at 955 cm^{-1} , while the equatorial C-O stretch lies at 1062 cm^{-1} [53]. Analysis of other OH and OCH_3 substituted cyclohexanes confirm these assignments by giving 1060-1070 cm^{-1} as the typical region for $\nu(\text{C-O})$ of an equatorial oxygen [54,55]. Therefore, these infrared studies suggest that I_1 and I_2 have equatorial and axial C-O bonds, respectively. Although infrared spectra of both unstable twist-boat and stable chair forms of cyclohexane suspended in solid Ar have been reported by Strauss [56], neither conformer has an absorption that is sufficiently characteristic to allow assignment of specific ring conformations to I_1 and I_2 based on the IR data alone. However, the possibility that I_1 or I_2 has unstable twist-boat conformation could virtually be ruled out on the basis of matrix warm-up experiments. No thermal $I_1 \rightleftharpoons I_2$ interconversion was observed at matrix temperatures as high as 30K, which is well above the temperature of approximately 20K required for fast (<1 min) isomerization of matrix

isolated species involving a barrier of around $0.7 \text{ kcal mol}^{-1}$ [28]. The latter is the estimated activation energy for twist-boat to chair interconversion of cyclohexyl radical, based on an experimental E_a value of 4 kcal mol^{-1} for the chair-to-chair flip given by Hori et al.[57] (which is thought to proceed through twist-boat conformations) and a molecular mechanics calculation on the ring inversion by Allinger [58]. Hence both cyclohexyl nitrite radical isomers have most probably chair conformation, I_1 with the C-O bond in the equatorial and I_2 in the axial position (Fig. 7).

As shown in Fig. 8, both diastereomeric O transfer paths lead to a transition state whose structure is close to that corresponding to the barrier between stable chair and unstable twist-boat minima. In this diagram, the ring inversion potential of cyclohexene oxirane biradical is approximated by that of cyclohexyl radical [57,58] (the small energy difference of $0.5 \text{ kcal mol}^{-1}$ between the equatorial and axial conformer of cyclohexanol [59] suggests small energy differences between equatorial and axial chair (or twist-boat) oxirane biradical isomers as well. This in turn implies that the relative energies of the biradical conformers may differ by no more than 10-20% from those of chair and twist-boat cyclohexyl radical). Therefore, as many as four diastereomeric oxirane biradicals could be formed, which are labelled CH-e, TB-a, CH-a, and TB-e in Fig. 8 ("e" indicates equatorial, "a" axial position of the C-O bond, respectively). Comparison of these with cyclohexyl nitrite radical stereoisomers I_1 and I_2 (Fig. 7) shows that I_1 is NO trapped cyclohexene oxirane biradical conformer CH-e, while I_2 is NO trapped CH-a. If the proposed approximation of the cyclohexene oxirane biradical potential by that of cyclohexyl radical is valid, the barrier for twist-boat to chair interconversion would be sufficiently high to allow trapping of any twist-boat (TB) cyclohexene oxirane biradical as TB nitrite radical, if it were formed. Since no TB cyclohexyl nitrite radical is observed, CH-e and CH-a are most likely the nascent conformations of cyclohexene oxirane biradical. The implication regarding the stereochemistry of O transfer to cyclohexene is that both diastereomeric reaction paths are pursued, each leading specifically to a particular oxirane biradical stereoisomer. A fraction of these is trapped as cyclohexyl nitrite radical (I_1 or I_2) by combination with NO cage neighbor, while the rest undergoes ring closure to yield

cyclohexene oxide. The apparent lack of formation of TB oxirane biradical may be due to relaxation of the initial half-chair nuclear configuration of the ring towards a chair form as the attacked C-atom undergoes $sp^2 \rightarrow sp^3$ rehybridization, regardless to which side of the C=C bond the oxygen is transferred.

In a similar investigation of red light induced reaction of cyclopentene-NO₂ pairs, we found again epoxide as exclusive final oxidation product that appeared concurrently with cyclopentyl nitrite radical [52]. In this case, only a single conformer of the radical was formed despite the fact that attack of the two sides of the CC double bond is expected to lead to diastereomeric cyclopentene oxirane biradicals. Trapping of a single radical conformer is rationalized in terms of the very low barrier to pseudorotation of the pentyl ring which permits relaxation to the most stable form even in the 12K environment.

Similar to the case of the ethylene + NO₂ reaction, irradiation of cyclohexene/NO₂/Ar matrices at wavelengths shorter than the 398 nm dissociation threshold led to additional final oxidation products aside from cyclohexene oxide. These are cyclohexanone and cyclohex-2-en-1-ol (cyclopentanone and cyclopent-2-en-1-ol in the case of cyclopentene + NO₂)[52]. Products were identified by comparison of product infrared spectra with those of authentic samples suspended in solid Ar. Photolysis experiments were conducted with the 355 nm output of a pulsed Nd: YAG laser or the 351-364 nm emission lines of a cw Ar ion laser, leading to results that were independent of the photolysis source. As can be seen from Fig. 9, the shapes of the absorbance growth curves point to distinct origins of the products. The cyclohexanone growth behavior is the same as that of cyclohexene oxide, but the growth kinetics of cyclohexenol is clearly different. This strongly suggests that cyclohexanone originates from the same reactant reservoir as cyclohexene oxide, i.e. the pool of cyclohexene-NO₂ collisional pairs that already undergo large amplitude O transfer upon excitation below the NO₂ dissociation limit. It indicates that upon 355 nm photolysis, epoxide and ketone are produced via a common ground state ¹D oxirane biradical

along the large amplitude O transfer path, consistent with the fact that the ketone is a 1,2-H shift product that can only originate from a singlet, but not from a triplet oxirane biradical [34,60]. On the other hand, the reactant reservoir that yields cyclohexenol must be substantially larger than the pool giving rise to epoxide and ketone according to the growth curves of Fig. 9. The only reactant that absorbs at 355 nm and whose reservoir exceeds that of alkene-NO₂ collisional pairs is isolated NO₂. Indeed, decreasing the reactant to matrix gas ratio (and hence the ratio of alkene-NO₂ pairs to isolated NO₂) increased the alcohol product relative to epoxide (ketone), confirming that cyclohexenol is produced by photochemistry of isolated NO₂. The reactant reservoir presumably involves NO₂ separated from a hydrocarbon molecule by one or several layers of Ar host atoms, as well as alkene-NO₂ cage pairs with unfavorable geometry to react along the large amplitude O transfer coordinate. Elementary reaction steps leading to cyclohex-2-en-1-ol are assumed to be addition of O(³P) to the alkene to yield triplet oxirane biradical, followed by elimination of H atom to give an ethanolate radical. Intramolecular 1,3-H shift of this transient monoradical to the more stable cyclohex-2-en-1-oxy radical tautomer, followed by combination with the cage H atom would produce the observed alcohol. In any event, this UV photolysis study of the cyclohexene + NO₂ system shows that straightforward infrared product analysis allows one to monitor large amplitude O transfer to the C=C bond independently from the NO₂ dissociation -O atom addition path.

Despite the evidence for reaction on the triplet surface, the fact that cycloalkene-NO₂ pairs excited at 355 nm generate typical singlet biradical products (epoxide and ketone) points to the intriguing possibility that even at energies above the dissociation limit there remains a substantial propensity for reactant pairs to couple into the large amplitude O transfer path rather than to proceed along the dissociation-oxygen atom addition path. In fact, there is a growing number of reports of bimolecular photochemical reactions of weak complexes in cryogenic matrices and in molecular beams that also suggest preferred coupling into large amplitude atom transfer coordinates

in cases where formation of free atoms would be energetically accessible, as will be discussed in sections IIB and III below.

3. Photooxidation of Allene and Alkynes

The visible light induced reactions of olefin-NO₂ pairs, discussed thus far, show that trapping of some fraction of the transient biradicals, formed upon oxygen transfer to the C=C bond, by NO furnishes a simple method for elucidation of regiochemical, stereochemical, and energy aspects of alkene photooxidations. This opened up the exciting prospect of obtaining insight into mechanism and dynamics of cumulene and CC triple bond oxidations which has long been sought after.

a. Allene + NO₂. Questions that can be explored by a study of oxygen transfer from NO₂ to allene are the competition between attack on the central and terminal carbon, and the structure of the transient(s) involved. The threshold to reaction of allene-NO₂ pairs was found at 585 nm [61]. Intense product absorptions at 1674 and 766 cm⁻¹, with ¹⁵N isotope shifts characteristic of NO double and single bond stretching modes, respectively, signalled formation of a nitrite radical. As can be seen from the infrared spectrum of this product in the region 2000-400 cm⁻¹, presented in Fig. 10a and Table 4, none of the absorptions appears as a doublet or a multiplet, which indicates that the radical emerges most probably as a single isomer. This conclusion is further corroborated by the fact that the observed cumulative ¹⁵N isotope frequency shift in the range 1700-700 cm⁻¹ of 1.036 is equal to the combined shift calculated for a ν(N=O) and a ν(N-O) mode (1.037, diatomic model). Fig. 10a exhibits the infrared difference spectrum obtained upon prolonged photolysis of allene-NO₂ pairs at 580 nm, while spectrum b of the same figure shows the effect of 6 minutes subsequent irradiation at 488 nm. Almost all of the

accumulated nitrite radical is depleted during this brief photolysis period with blue light, namely by elimination of NO to yield allene oxide and cyclopropanone according to infrared analysis based on ^{18}O and perdeuterated modifications. Infrared matrix spectra of these molecules have previously been reported by Singmaster and Pimentel [62]. Of the two conceivable structures of the nitrite radical, $\text{CH}_2=\text{C}(\text{ONO})-\dot{\text{C}}\text{H}_2$ and $\text{CH}_2=\dot{\text{C}}-\text{CH}_2-\text{ONO}$, both could yield allene oxide upon ring closure following expulsion of NO, but only the isomer with the nitrite group at the central carbon could act as a precursor of cyclopropanone. Since only a single nitrite radical isomer is observed, detection of cyclopropanone as secondary photolysis product strongly suggests that the nitrite radical has $\text{CH}_2=\text{C}(\text{ONO})-\dot{\text{C}}\text{H}_2$ structure. An empirical mode assignment of the infrared spectrum of this new radical based on the matrix infrared spectrum of allyl radical [63] is given in the detailed report [61].

By analogy with the large amplitude oxygen transfer mechanism which we have independently established for visible light induced NO_2 + alkene (Sect. A1) and NO_2 + alkyne reactions (discussed below), it is reasonable to assume that photo-initiated chemistry of allene- NO_2 pairs also involves transfer of O to the multiple bond to yield a transient biradical in a single step. As indicated in Scheme VIII, detection of a nitrite radical with the structure $\text{CH}_2=\text{C}(\text{ONO})-\dot{\text{C}}\text{H}_2$ as the sole trapped intermediate implies that oxygen attack occurs exclusively at the central carbon leading to the biradical $\text{CH}_2=\text{C}(\dot{\text{O}})-\dot{\text{C}}\text{H}_2$. Hence the regiochemistry of this oxidation reaction can again readily be deduced from the structure of the observed nitrite radical.

The absence of the $\text{CH}_2=\dot{\text{C}}-\text{CH}_2-\text{ONO}$ isomer, and hence that of transient $\text{CH}_2=\dot{\text{C}}-\text{CH}_2-\dot{\text{O}}$ can be rationalized by aid of the potential energy diagram of the allene + NO_2 system. According to the diagram shown in Fig. 11, even at 488 nm, the shortest wavelength used to excite allene- NO_2 collisional pairs, photons do not have sufficient energy to reach the ground electronic state of 1-allenylidoxo biradical $\text{CH}_2=\dot{\text{C}}-\text{CH}_2-\dot{\text{O}}$ ($\tilde{\text{X}}^3\text{A}''$). By contrast, light quanta corresponding to the threshold wavelength of 585 nm excite the reactant pairs to levels about 30 kcal mol $^{-1}$ above

the $\tilde{X}^3B_2$ ground state of the much more stable 2-allenyldoxy biradical $\dot{C}H_2CO\dot{C}H_2$. Ground state energies of these biradicals were taken from recent ab initio results of Lester and coworkers [64]. We therefore conclude that the complete regioselectivity of the allene + NO_2 reaction can be understood simply on the basis of the energetics of the transient photoproduct. The higher stability of $\dot{C}H_2CO\dot{C}H_2$ compared with $CH_2\dot{C}CH_2\dot{O}$ lies in the inability of the latter to form a CO double bond [64].

Ab initio energies of the lowest three excited electronic states of CH_2COCH_2 biradical (1A_1 , 3B_1 , and 1B_1) have been reported but Morokuma and collaborators [65] and are included in Fig. 11. Interestingly, the $CH_2=C(\dot{O})-\dot{C}H_2$ electronic structure of the biradical inferred from the infrared spectrum of the observed nitrite radical corresponds to the electron configuration of the (singlet or triplet) B_1 excited state. By contrast, the lower lying 1A_1 and $\tilde{X}^3B_2$ states of the biradical have a CO double bond and a lone electron on each methylene carbon ($\dot{C}H_2-C(=O)-\dot{C}H_2$), hence, if formed, would combine with NO to yield a nitroso radical but not a nitrite radical. However, no nitroso species is found. In the higher lying 1B_1 and 3B_1 states CH_2COCH_2 has a singly occupied oxygen p-orbital and hence is expected to form a nitrite radical upon combination with NO cage neighbor, as observed (that NO combination at the allyl moiety to form a nitroso C-N bond is not competitive with N-O bond formation is consistent with our results in the case of NO_2 + alkene photochemistry where NO was found to react with the O rather than the C radical center in every case (Sects. A1 and A2)). Therefore, the structure of the observed nitrite radical suggests that O transfer from NO_2 to allene yields 2-allenyldoxy biradical in the singlet or triplet B_1 excited state (both are allowed under the conservation of spin principle). This would imply that combination of NO to form nitrite radical is fast on the timescale of internal conversion or intersystem crossing to the lower lying 1A_1 or 3B_2 state.

Indeed, preferred coupling of the visible light excited NO_2 -allene pairs into the $CH_2COCH_2(B_1)$ state rather than the 1A_1 or 3B_2 state is consistent with electronic state

correlations. Assuming $\text{N-O}\cdots\text{C}=\text{C}=\text{C}$ as the reaction plane as basis for establishing a Salem correlation diagram [66], one finds that ground state NO_2 ($^2\text{A}_1$)- $\text{C}_3\text{H}_4(\text{S}_0)$ pairs correlate with $\text{CH}_2\text{COCH}_2(\text{B}_1) + \text{NO}(^2\pi)$, but not with $^1\text{A}_1$ or $\tilde{\text{X}}^3\text{B}_2$ biradical states [61]. Correlations of the $^2\text{A}_1$ state, which involve strongly avoided crossings, are relevant here because NO_2 excited at visible wavelengths is a highly vibrationally excited species with mixed $^2\text{B}_2$ - $^2\text{A}_1$ electronic parentage with the latter dominating (Sect. A1 and Ref. [37]).

As can be seen from Fig. 11, interpretation of our results in terms of $^1\text{B}_1$ (or $^3\text{B}_1$) as the nascent biradical electronic state is supported by the observed threshold to reaction at 585 nm. Both lower lying $^1\text{A}_1$ and $^3\text{B}_2$ states would be accessible energetically by photolysis with light deep in the near infrared (NO_2 absorbs at wavelengths as long as 1000 nm [39]), yet no reaction is observed at these photon energies. The biradical is expected to emerge in the unstable, twisted C_s conformation if no adjustment of the dihedral angle of allene occurs during the oxygen transfer. In fact, the C_s form of the $^1\text{B}_1$ state would be suitable for adiabatic ring closure to allene oxide, yet kinetic analysis of the allene oxide (and cyclopropanone) absorbance growth indicates that neither final oxidation product is formed upon (single photon) excitation of allene- NO_2 pairs, only by secondary photolysis of the nitrite radical [61]. Hence $\text{CH}_2\text{COCH}_2(\text{B}_1)$ biradical is quantitatively trapped as a nitrite radical, presumably because ring closure of the C_s conformer is slow on the timescale to relaxation to the approximately 8 kcal mol^{-1} more stable planar C_{2v} form (in Fig. 11, an 8 kcal mol^{-1} energy difference between C_s and C_{2v} forms of $\tilde{\text{X}}^3\text{B}_2$ biradical was assumed to hold for all states, which is certainly an oversimplification).

It is interesting to contrast the energy path of the photoinitiated $\text{NO}_2 + \text{allene}$ reaction with $\text{O}(^3\text{P}) + \text{CH}_2=\text{C}=\text{CH}_2$ under single collision conditions in a crossed molecular beam. Lee and coworkers inferred from angular distributions and time-of-flight mass spectra of products that the oxygen atom addition involves in its initial step branching between triplet ground state

$\dot{\text{C}}\text{H}_2\text{C}(\text{O})\dot{\text{C}}\text{H}_2$ and $\text{CH}_2\dot{\text{C}}\text{CH}_2\dot{\text{O}}$ biradical corresponding to attack on the central and terminal carbon, respectively [67].

b. Alkyne + NO₂. Of particular interest was trapping of transients that may be formed upon photo-induced reaction of alkyne-NO₂ collisional pairs since none has thus far been observed upon O transfer to a CC triple bond by any technique. We will review in this section the results of our study of acetylene, methylacetylene, and dimethylacetylene photooxidation by NO₂. Since the $\text{CH}_3\text{-C}\equiv\text{C-CH}_3\text{+NO}_2$ system furnished the key to the mechanism of triple bond oxidation, it will be discussed first.

The threshold to single photon induced oxygen transfer of dimethylacetylene-NO₂ pairs was found at 610 nm, with dimethylketene as the sole final oxidation product [61]. Identification of the ketene was based on a product absorption at 2130 cm⁻¹ which is characteristic for the asymmetric C=C=O stretching mode both with respect to frequency [68] and ¹⁸O shift (26 cm⁻¹) [69]. As can be seen from the infrared spectrum obtained upon prolonged photolysis of $\text{CH}_3\text{-C}\equiv\text{C-CH}_3\text{-NO}_2$ pairs at 585 nm, Fig. 12, this absorption appears as a multiplet with bands ranging from 2136 to 2104 cm⁻¹, a splitting that was also noted in the case of dimethylketene produced by photodissociation of the corresponding α -diazoketone [70]. The spectrum of Fig. 12 contains an additional product aside from $(\text{CH}_3)_2\text{C=C=O}$ and NO, with most absorptions split into several bands as can be seen clearly from the expanded spectra in Fig. 13. Strong features around 1710 cm⁻¹ and in the 1600-1550 cm⁻¹ range exhibit ¹⁸O and ¹⁵N isotope frequency shifts that are characteristic for weakly coupled C=O and C=N stretching modes, respectively, as can be seen from the full list of observed bands of parent, ¹⁵N, and ¹⁸O modification presented in Table 5. In fact, $\nu(\text{C=N})$ bands in the 1600-1550 cm⁻¹ region are typical for the double bond (out-of-phase) stretching mode of the C=N-O group found in nitrones [72]. This assignment is further supported by the intense multiplet between 1300 and 1260 cm⁻¹, a region where the nitron N-O (in-phase)

stretching mode is expected to absorb [72]. The only species containing a C=O and a C=N-O group that could conceivably be formed upon reaction of dimethylacetylene with NO₂ is acetyl methyl iminoxy radical $\text{CH}_3\text{-C(=O)-C(=N-\dot{\text{O}})\text{-CH}_3$. Although no vibrational spectra of this or any other iminoxy radical had previously been reported, earlier ESR spectroscopic studies of acetyl methyl iminoxy radical in solution by Gilbert et al. suggest that it exists as a mixture of several isomers shown in Scheme IX, namely stable s-trans and unstable s-cis forms with respect to the C-C bond, each having the additional possibility of cis (syn) and trans (anti) configuration of the iminoxy oxygen [73].

Wavelength selective photo-interconversion experiments allowed us to test whether this isomerism is responsible for the observed multiple splittings of iminoxy radical absorptions. Close-ups of infrared difference spectra presented in Fig. 13b show the effect of 3 minutes irradiation at 514 nm of a matrix in which iminoxy radical had first been accumulated by prolonged photolysis of dimethylacetylene-NO₂ pairs at 585 nm. During such brief photolysis with green light dimethylacetylene + NO₂ reaction can be neglected, hence the absorbance changes of Fig. 13b are exclusively due to interconversion of iminoxy radical species. Comparison of spectra a and b of the figure reveals three distinct spectra, namely a decreasing set of bands (I_A), a spectrum that grows in (I_{B1}), and a set of bands I_{B2} that show only very little absorbance change. Most bands of species I_{B1} and I_{B2} are very close in frequency and are therefore listed in Table 5 separately from those of I_A . The mere fact that absorptions of I_A , I_{B1} and I_{B2} exhibit similar but not identical ¹⁵N and ¹⁸O isotope shifts strongly suggests that these species are diastereomers, most probably with structures shown in Scheme IX.

The key to a more specific structural assignment of I_A , I_{B1} , and I_{B2} was the matrix infrared spectrum of the corresponding (closed shell) oxime $\text{CH}_3\text{-C(=O)-C(=N-OH)\text{-CH}_3$ (diacetyl monoxime). Selective s-trans to s-cis interconversion in solid Ar with UV lasers allowed us to assign the infrared spectra of the two forms of this molecule [61]. Comparison with the iminoxy

radical product spectra revealed that I_A has cis, I_{B1} and I_{B2} trans conformation about the C-C bond. The closeness of the I_{B1} and I_{B2} bands suggests that the two isomers differ in their configuration with respect to the iminoxy oxygen, although a specific assignment of the configuration (cis or trans) lies beyond the present data. Even the s-cis iminoxy radical I_A appears to be formed as a cis and a trans (C=N) isomer (Scheme IX). As can be seen from Table 5, the I_A spectrum contains closely spaced absorptions that have significantly different ^{15}N and ^{18}O isotope shifts, indicating that these are not site splittings (e.g. the doublet at 1560.3 cm^{-1} (^{15}N shift of 28.1 cm^{-1}) and 1545.3 cm^{-1} (21.4 cm^{-1}), or the doublet at 1258.0 cm^{-1} (0 cm^{-1}) and 1239.6 cm^{-1} (7.6 cm^{-1})). Moreover, the cumulative ^{15}N isotope frequency shifts of I_A bands in the $1500\text{--}400\text{ cm}^{-1}$ range is 1.032, which is about twice as large as the 1.013 shift of I_{B1} absorptions, and the 1.016 shift of the I_{B2} bands in that region (1.018 is the $\nu(^{15}\text{N-O})$ shift predicted by the diatomic oscillator model).

Two observations showed that visible light induced reaction of NO_2 -alkyne pairs involves oxygen transfer to yield a transient biradical that is either stabilized by formation of ketene or iminoxy radical. First, while the branching ratio between ketene and iminoxy radical was 0.1 for dimethylacetylene + NO_2 , it increased to 1.1 for methylacetylene + NO_2 , and ≥ 20 for acetylene + NO_2 [74]. Second, this branching was three times smaller for $\text{C}_2\text{D}_2 + \text{NO}_2$ than for $\text{C}_2\text{H}_2 + \text{NO}_2$ (see below). The CH_3 group and the D isotope effect on the competition between ketene and iminoxy radical formation both constitute strong evidence that the two products share a common precursor. The only common transient species preceding ketene and iminoxy radical that we can conceive of is a ketocarbene biradical, shown in Scheme X (the term biradical defined as an even-electron species that has one bond less than the number permitted by the standard rules of valence [66,75]).

Details of the energy path of oxygen transfer to CC triple bonds can be inferred from the structure of the observed iminoxy radical in conjunction with ab initio results on the HCC(O)H

biradical reported recently by several groups. The potential energy diagram presented in Fig. 14 shows low lying states of $\text{CH}_3\text{CC}(\text{O})\text{CH}_3$ biradical and energies of the final products of the dimethylacetylene + NO_2 reaction. The energy of electronic ground state $\text{CH}_3\ddot{\text{C}}\text{C}(\text{O})\text{CH}_3$ relative to that of $\text{CH}_3\text{C}\equiv\text{CCH}_3 + \text{NO}_2$ was derived from the ab initio value of the potential energy change for $\text{O}(^3\text{P}) + \text{HC}\equiv\text{CH} \rightarrow \text{H}\ddot{\text{C}}\text{C}(\text{O})\text{H}(\tilde{\text{X}})$ reported by Harding [76]. The energies of the lowest three excited states of $\text{CH}_3\text{CC}(\text{O})\text{CH}_3$ biradical displayed in Fig. 14 are the ab initio energies of the corresponding $\text{HCC}(\text{O})\text{H}$ states (relative to $\text{H}\ddot{\text{C}}\text{C}(\text{O})\text{H}(\tilde{\text{X}})$) given by Harding [76] and Bargon and Yoshimine [77,78]. Use of $\text{HCC}(\text{O})\text{H}$ energies is justified by the result of semiempirical calculations by Bachmann et al. which showed that energies of singlet excited ketocarbenes $\text{CH}_3\ddot{\text{C}}\text{C}(\text{O})\text{CH}_3$ and $\text{H}\ddot{\text{C}}\text{C}(\text{O})\text{H}$ (relative to the respective ground states) are within less than 5 kcal mol⁻¹ of each other [79], which is well within the uncertainty of the $\text{H}\ddot{\text{C}}\text{C}(\text{O})\text{H}(\tilde{\text{X}})$ energy estimate itself [76]. According to the theoretical work, the triplet ground state ($^3\text{A}''(\sigma_c\pi_c)$) and the first excited singlet state ($^1\text{A}'(\sigma_c^2)$) of the biradical have both a ketocarbene electron configuration with a CO double bond, a central CC single bond, and a carbene C, as shown in Fig. 14 (symbols in parenthesis indicate orbitals occupied by non-bonding electrons. σ means in-plane (sp^2), π perpendicular (p) orbital with respect to the CCO plane). In contrast to these two lowest states, the two next higher states of the biradical that are energetically accessible upon long wavelength visible light induced O transfer to dimethylacetylene have an electron configuration corresponding to a 1,3-biradical ($\text{CH}_3-\dot{\text{C}}=\text{C}(-\dot{\text{O}})-\text{CH}_3$), designated $^1\text{A}'(\sigma_c\sigma_o)$ and $^3\text{A}'(\sigma_c\sigma_o)$ in Fig. 14. 1,2-migration (Wolff rearrangement) that leads to ketene is expected to occur in a state with a very low barrier for this process as it has to compete with activationless combination with NO cage neighbor. The ab initio results on $\text{HCC}(\text{O})\text{H}$ indicate that the barriers to 1,2-migration in the triplet states ($^3\text{A}'(\sigma_c\sigma_o)$ and $\tilde{\text{X}}^3\text{A}''(\sigma_c\pi_c)$) are far too high to be accessible in our experiment (the ketocarbene-ketene rearrangement barrier for $^3\text{A}''(\sigma_c\pi_c)$ is shown in Fig.14), and that the lowest energy path from the $^1\text{A}'(\sigma_c\sigma_o)$ state to ketene proceeds through the $^1\text{A}'(\sigma_c^2)$ ketocarbene state. This leaves $^1\text{A}'(\sigma_c^2)$ as the most likely state in which 1,2- CH_3 group migration takes place. The fact that $\text{CH}_3\text{CC}(\text{O})\text{CH}_3$ biradical is trapped as an iminoxy radical with a s-cis to s-trans

conformational ratio (I_A/I_B) close to one indicates that the transient reacts with NO coproduct in this same $^1A'(\sigma_c^2)$ state. First, trapping of $\text{CH}_3\ddot{\text{C}}\text{C}(\text{O})\text{CH}_3$ by NO in a 1,3-biradical state would yield either a radical with a nitrite (ONO) functional group if NO would combine at the O radical center, or an iminoxy radical with predominantly s-cis conformation (I_A) if NO were to react at the carbon, neither of which is observed [61]. Furthermore, Bodot, Pourcin and their collaborators have recently shown that $\text{CH}_3-\ddot{\text{C}}-\text{C}(=\text{O})-\text{CH}_3$, produced by photodissociation of the corresponding α -diazoketone $\text{CH}_3-\text{C}(=\text{N}_2)-\text{C}(=\text{O})-\text{CH}_3$ in a rare gas matrix is trapped by CO in its $^1A'(\sigma_c^2)$ state to yield ketoketene [79]. Since NO is certainly no less efficient than CO in trapping the ketocarbene, there is little doubt that NO reacts with $\text{CH}_3\ddot{\text{C}}\text{C}(\text{O})\text{CH}_3(^1A'(\sigma_c^2))$ before it undergoes intersystem crossing to the $^3A''(\sigma_c\pi_c)$ ground state. Second, in the equilibrium structure of the $^1A'(\sigma_c^2)$ state the $\ddot{\text{C}}-\text{H}(\ddot{\text{C}}-\text{CH}_3)$ bond is approximately perpendicular to the CCO plane according to ab initio work on $\text{H}\ddot{\text{C}}\text{C}(\text{O})\text{H}$ [77,78,80] and semiempirical calculations on $\text{CH}_3\ddot{\text{C}}\text{C}(\text{O})\text{CH}_3$ [79]. Upon CN bond formation the $\text{CH}_3\text{C}(=\text{N}\dot{\text{O}})$ group would have about equal opportunity to flip either way to yield s-cis or s-trans (CC) radical giving similar yields of I_A and I_B , as observed. Hence $^1A'(\sigma_c^2)$ is the most probable state in which branching between CH_3 group shift and combination with NO cage neighbor occurs (Scheme X) (the distribution between I_{B1} and I_{B2} (and corresponding I_{A1} and I_{A2} forms that differ in the position of the iminoxy oxygen) presumably depends on the exact orientation of NO relative to the $\text{CH}_3\ddot{\text{C}}\text{C}(\text{O})\text{CH}_3$ transient prior to combination with the carbene C).

An intriguing aspect of this system is that $\text{NO}_2(^2A_1) + \text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3 (S_0)$ does not correlate with $\text{CH}_3\ddot{\text{C}}\text{C}(\text{O})\text{CH}_3(^1A'(\sigma_c^2)) + \text{NO}(^2\pi)$ according to the corresponding Salem diagram, hence the state in which competition between CH_3 group migration and combination with NO takes place is most probably not the nascent state of the transient. However, correlation exists between reactant states and the $^1A'(\sigma_c\sigma_o)$ biradical state. This state is expected to be strongly coupled with the $^1A'(\sigma_c^2)$ state because the two have the same symmetry and are very close in energy, implying that the $^1A'(\sigma_c\sigma_o)$ state may be extremely short lived. Therefore, the most likely reaction path is O

transfer to the CC triple bond to yield $\text{CH}_3\text{CC}(\text{O})\text{CH}_3$ in the $^1\text{A}'(\sigma_c\sigma_o)$ state, followed by relaxation to the $^1\text{A}'(\sigma_c^2)$ state fast on the timescale of combination with NO. This is the first insight into O transfer to a $\text{C}\equiv\text{C}$ bond gained by chemical trapping of an electronically excited biradical.

It is interesting to note that $\text{CH}_3-\dot{\text{C}}=\text{C}(-\dot{\text{O}})-\text{CH}_3$ ($^1\text{A}'(\sigma_c\sigma_o)$) is ring-opened dimethyloxirene, $\text{CH}_3-\overline{\text{C}}=\text{C}(-\dot{\text{O}})-\text{CH}_3$, yet this elusive molecule is not formed despite that fact that red light induced O transfer would produce it with the least amount of excess internal kinetic energy (Fig. 14). This speaks against dimethyloxirene being a genuine minimum on the potential energy surface, a question that is still a matter of controversy [61, 79,81].

Similar to the case of alkene oxidations, this study suggests that oxygen transfer to the $\text{C}\equiv\text{C}$ bond is asymmetric, leading to a biradical intermediate rather than to oxirene through O atom insertion as has occasionally been speculated [82,83]. Reaction on the singlet $\text{CH}_3\text{CC}(\text{O})\text{CH}_3$ biradical hypersurface directly accessed by large amplitude O transfer from NO_2 may be typical for alkyne oxidation by common closed shell oxidizers like peroxy acids.

This new way of determining alkyne oxidation paths allowed us to explore the regiochemistry of O transfer to an unsymmetrically substituted CC triple bond. As shown the Scheme XI, in the case of the simplest unsymmetrical alkyne, methylacetylene, oxygen atom attack could occur at the central or at the terminal carbon. However, the expected final oxidation product $\text{CH}_3\text{C}(\text{H})=\text{C}=\text{O}$ would not carry any signature as to the branching between the two regiochemical paths. Single photon excitation of $\text{CH}_3\text{C}\equiv\text{CH}\cdot\text{NO}_2$ collisional pairs in solid Ar with long wavelength visible light produced both methylketene and iminoxy radical (Scheme XI), the latter signalled by multiplets in the $1720\text{-}1700\text{ cm}^{-1}$ ($\nu(\text{C}=\text{O})$) and $1590\text{-}1570\text{ cm}^{-1}$ ($\nu(\text{C}=\text{N})$) regions [74]. Selective irradiation of iminoxy radical at various visible wavelengths revealed the presence

of four isomers, all of which were photo-interconvertible [74]. This indicates that all iminoxy radical species are rotational isomers either of radical 1' or of radical 2' displayed in Scheme XI, but not of both. In other words, only one of the two possible constitutional isomers 1' and 2' appears to be produced. Frequency shifts of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ absorptions observed upon selective D substitution of CH_3 and CH groups allowed us to find out which isomer was formed. In the case of $\text{CH}_3\text{-C}\equiv\text{C-D} + \text{NO}_2$, all $\nu(\text{C}=\text{O})$ modes of the resulting iminoxy radical exhibited a substantial shift of $6\text{-}9\text{ cm}^{-1}$. By contrast, radicals formed upon O transfer to $\text{CD}_3\text{-C}\equiv\text{C-H}$ showed much smaller $\nu(\text{C}=\text{O})$ shifts of less than 2 cm^{-1} . Infrared data on partially deuterated acetaldehyde [84] and other small carbonyls indicate that D substitution of aldehydic hydrogen has a much larger effect on the $\nu(\text{C}=\text{O})$ frequency than substitution of the methyl hydrogens. This strongly suggests that the observed radical is formyl methyl iminoxy radical 1' (Scheme XI). The various rotational isomers have structures analogous to those of acetyl methyl iminoxy radical shown in Scheme IX. This assignment is corroborated by detection of propynol as a photodissociation product of the trapped iminoxy radical, which can only originate from isomer 1' but not 2'. Hence the ketocarbene trapping method allowed us to establish that the reaction is completely regioselective, resulting exclusively in oxygen transfer to the terminal carbon of methylacetylene. We attribute the regioselectivity to the higher stability of ketocarbene 1 compared to the isomer 2, with the consequence that photo-excited $\text{CH}_3\text{-C}\equiv\text{C-H}\cdot\text{NO}_2$ pairs couple preferentially into $\text{CH}_3\text{CC(O)H} + \text{NO}$ rather than $\text{CH}_3\text{C(O)CH} + \text{NO}$ product states. This is fully corroborated by the observed photooxidation thresholds for methylacetylene, dimethylacetylene, and unsubstituted acetylene. The $\text{CH}_3\text{-C}\equiv\text{C-H} + \text{NO}_2$ threshold wavelength is 610 nm, which is identical with that of $\text{CH}_3\text{-C}\equiv\text{C-CH}_3 + \text{NO}_2$ that leads to the CH_3 substituted carbene $\text{CH}_3\text{-}\ddot{\text{C}}\text{-C(=O)-CH}_3$ (similar to 1), but very different from the $\text{H-C}\equiv\text{C-H} + \text{NO}_2$ threshold of 550 nm which leads to unsubstituted carbene $\text{H-}\ddot{\text{C}}\text{-C(=O)-H}$ (similar to 2) [74].

Interestingly, large amplitude oxygen transfer of $\text{HC}\equiv\text{CH}\cdot\text{NO}_2$ pairs that can be induced with light at 550 nm and shorter wavelengths gives $\text{CH}_2=\text{C}=\text{O} + \text{NO}$ as exclusive products. No iminoxy radical is trapped [74]. This implies that Wolff rearrangement of singlet $\text{H}-\ddot{\text{C}}-\text{C}(=\text{O})-\text{H}$ ($^1\text{A}'(\sigma_c^2)$) is fast even on the timescale of combination with NO, consistent with the fact that most ab initio calculations report no barrier for rearrangement to ketene [77,78,80]. While large amplitude O transfer from NO_2 to acetylene accesses exclusively the excited singlet $\text{HCC}(\text{O})\text{H}$ surface, Lee and his group have shown that under single collision conditions in a crossed molecular beam $\text{O}(^3\text{P}) + \text{HC}\equiv\text{CH}$ proceeds on the triplet ground state surface throughout leading to Wolff rearrangement as well as H atom elimination [85]. This example demonstrates more convincingly than any other that the NO coproduct of the matrix reaction, even though a radical itself, does not effect intersystem crossing of $\text{H}\ddot{\text{C}}\text{C}(\text{O})\text{H}$ ($^1\text{A}'(\sigma_c^2)$) to the lower lying triplet ground state. The latter would certainly be trapped as an iminoxy radical because of the large barrier to 1,2-H shift, yet none is observed. All hydrocarbon photooxidations by NO_2 conducted thus far indicate that continued chemistry of transient biradicals is always fast on the timescale of ^2NO induced singlet-triplet state coupling.

B. Ozone as Oxygen Donor

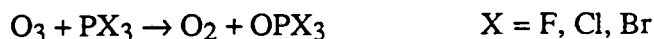
Ozone is best known for its role in atmospheric chemistry [86] and in oxidation of organic molecules [87]. The matrix isolation technique has played a role in both areas, most recently reviewed in the case of atmospheric chemistry by Almond and Downs [8]. Trapping of intermediates formed upon reaction of organic molecules with O_3 has added significantly to the understanding of the mechanism of corresponding gas and solution phase reactions, principally through the work of Günthard [23,88,89], Andrews [90-92], and Nelandar [93]. The main role of O_3 in matrix work, however, has been that of a photochemical oxygen transfer agent for generation of new chemical species. Ozone has a very intense optical absorption between 200 and 300 nm

with a maximum at 255 nm (Hartley band), adjoined by a weak tail extending to 360 nm (Huggins bands) [38]. At even longer wavelengths the spectrum features an absorption that spans from 450 to 800 nm with a peak around 600 nm (Chappuis bands). This absorption is about 2000 times less intense than the 250 nm band [38]. Since all absorptions are situated well above the 9100 cm^{-1} dissociation limit to $\text{O}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$ ground state fragments [38], it is natural to envision visible or UV light induced oxidation by O_3 in a matrix as a two step process in which ozone dissociates to atomic oxygen which subsequently adds to the substrate molecule. Energetics dictates that predissociation from the $^1\text{B}_1$ excited state presumed to be accessed upon irradiation of the Chappuis bands [94-97] can exclusively lead to ground state $\text{O}(^3\text{P})$. By contrast, dissociation of $\text{O}_3(^1\text{B}_2)$ prepared upon excitation of the Hartley band is known to yield predominantly excited $\text{O}(^1\text{D})$ and $\text{O}_2(^1\Delta_g)$ in the gas phase [38]. Differences in chemical products observed upon visible versus UV photolysis of O_3 -substrate complexes in matrices have therefore occasionally been attributed to $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ involvement, respectively [3].

While studying photo-induced oxygen transfer of weak complexes like $\text{O}_3\cdot\text{PH}_3$ [98,99], $\text{O}_3\cdot\text{AsH}_3$ [100], $\text{O}_3\cdot\text{P}_4$ [101], $\text{O}_3\cdot\text{PX}_3$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}$, [102]), $\text{O}_3\cdot\text{SbH}_3$ [103], and $\text{O}_3\cdot\text{GeH}_4$ [104] in rare gas matrices with the goal of generating new species, Andrews was the first to notice high efficiencies of red light induced reaction that cannot be reconciled with a mechanism that involves sequential steps of O_3 dissociation and free $\text{O}(^3\text{P})$ addition. Since the weak complexes of ozone with these substrate molecules exhibit distinct absorptions that are separated from those of the isolated reactants, typically by several cm^{-1} (notably $\nu_3(\text{O}_3)$ [105,106]), the photolysis behavior of complexes and of isolated O_3 present in the same matrix could be monitored independently. Interestingly, no dissociation of isolated O_3 was observed under the same red light irradiation that resulted in reaction of the complexes. Only upon excitation of the 250 nm UV band did photolysis of isolated ozone occur. Visible spectra of matrices containing O_3 -substrate complexes exhibited no features other than the Chappuis bands observed in the case of O_3 /rare gas matrices. In

particular, no bands or intensity changes were noted that would point to a charge transfer absorption of the weak complex.

In their most detailed study of the wavelength dependence of the photochemistry of weak ozone complexes, Andrews and coworkers monitored the yield of the primary photoproducts $OPX_3 + O_2$ upon irradiation of matrices $PX_3/O_3/Ar$ with filtered Hg arc radiation [102].



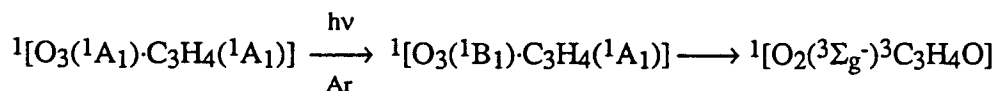
Phosphorous halide growth was measured by the growth of its intense $\nu(C=O)$ absorption. Using this infrared monitoring technique, substantial differences in the efficiency of red light initiated oxygen transfer were found among the three phosphorus halides. The $PCl_3 \cdot O_3$ complex was four times more reactive than $PBr_3 \cdot O_3$, and 10 times more reactive than $PF_3 \cdot O_3$. The most interesting finding was, however, that for all three complexes the OPX_3 product growth observed upon irradiation with visible light came surprisingly close to that obtained upon UV photolysis: OPX_3 yields upon visible light photolysis were 90% ($O_3 \cdot PCl_3$), 50% ($O_3 \cdot PBr_3$), and 10% ($O_3 \cdot PF_3$) of those measured when exciting by light that covered both the UV and visible region [102]. Since the 250 nm band of O_3 is over three orders of magnitude more intense than the visible absorption, this indicates that excitation of the Chappuis bands of $O_3 \cdot PX_3$ complexes may be substantially more efficient in inducing O transfer than excitation of the Hartley band. Free $O(^3P)$, if it were produced upon irradiation of the 1B_1 state with red photons is expected to react less efficiently with PX_3 than excited $O(^1D)$ atoms that may emerge from $O_3(^1B_2)$, contrary to what is observed. Instead, the unexpected high efficiency of red light in effecting O transfer points to direct coupling of photo-excited $O_3(^1B_1) \cdot PX_3$ reactant states into $O_2(^1\Delta) \cdot OPX_3(S_0)$ product states via an asymmetric O-O-P large amplitude stretching mode (singlet excited O_2 is the most probable primary photoproduct state according to the conservation of spin rule [102]). This is fundamentally no different from direct coupling of NO_2 -alkene pairs, excited to bound or

predissociative vibronic levels, into oxirane biradical + NO product states via the asymmetric N-O-C large amplitude coordinate (Sect. A), but contrasts sharply with an O₃ dissociation - O(³P) addition sequence of steps. A possible reason for the reduced efficiency upon excitation of the Hartley band is preferential coupling of O₃(¹B₂) into O + O₂ rather than OPX₃ + O₂ product states. Thermal reaction of O atoms so produced with PX₃ cage neighbor may be less efficient than direct coupling of excited O₃·PX₃ reactant states into OPX₃ + O₂ product states via large amplitude O transfer. In any case, the results of the red light induced O transfer of the weak ozone complexes point to a reaction path that is dictated by O₃(¹B₁)-PX₃ → OPX₃ + O₂ electronic state correlations rather than merely by the reactivity of the O(³P) + PX₃ → OPX₃ system.

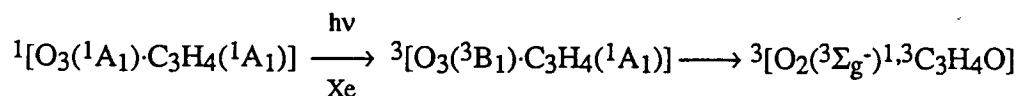
In their study of red light induced reaction of ozone with allene in solid Ar, Kr, and Xe, Singmaster and Pimentel made observations that also suggest that excited O₃-substrate reactant states control the outcome of the chemistry rather than simply the reactivity of O(³P) towards allene [62]. Suspensions of allene and O₃ in the solid rare gases were irradiated with a beam containing the two emission lines of a Kr ion laser (647 nm (85%), 676 nm (15%)), and the chemistry monitored by infrared spectroscopy. Major products observed were acrolein (both in the s-cis and s-trans form), cyclopropanone, and allene oxide, the latter synthesized by this technique for the first time. Absorptions of $\text{CH}_2=\overline{\text{C}}-\text{CH}_2-\text{O}$ were found at 3250 cm⁻¹ (ν(C-H)), 1823 cm⁻¹ (ν(C=C)), 1109 cm⁻¹ (ν(C-O), γ_r(CH₂)), 881 cm⁻¹ (ring breathing), and 794 cm⁻¹ (=CH₂wag). The assignments were based on ¹⁸O and D isotope shifts, and on comparison with vibrational spectra of epoxides [62]. Ethylene, CO, ketene, and formaldehyde appeared as minor products.

The most interesting finding of this study was a substantial change of the branching among the major photolysis products when Ar was replaced by Xe. As can readily be seen from Fig. 15, the branching ratio cyclopropanone/acrolein increases substantially in favor of the ring product

from Ar to Xe, by a factor of 2.5 according to integrated intensity measurements. In addition, growth rates in Xe were found to be eight times higher than in Ar. The latter can be accounted for, at least in part, by a four-fold larger cross section of the red absorption of ozone/allene suspensions in Xe than in Ar [62]. The visible electronic spectrum of matrices containing allene-ozone pairs and isolated ozone exhibited only the Chappuis bands of O₃. The larger absorption cross section in Xe was explained by the external heavy atom spin-orbit effect of the matrix environment that may enhance absorption into one or possibly all three excited triplet states of ozone that are clustered around the ¹B₁ state [94-96]. With this assumption, the different product branchings in Ar and Xe can be interpreted by access to excited triplet surface (or surfaces) in Xe but not in Ar. According to the preferred explanation proposed by the authors, absorption of red light by O₃:allene pairs in solid Ar would prepare O₃ predominantly in the excited ¹B₁ state, hence conservation of spin along the reaction path would force the primary biradical into a triplet state.



By contrast, in solid Xe a substantial fraction of ozone may be prepared in a triplet excited state (e.g. ³B₁ [96]), hence singlet primary biradical states would become accessible in this case.



Consideration of the reactant and product state energies reveals that a singlet C₃H₄O biradical state can be reached from the red light excited allene-O₃ pairs that corresponds to a cyclopropanone excited state. This may explain the enhanced yield of the ring product when the reaction is initiated in Xe. In the absence of access to singlet biradical states, as in the case of Ar, O₃:allene pairs apparently couple into triplet excited biradical states of the more stable acrolein. Similar to

Andrews' systems and to the NO_2 reactions, one can envision large amplitude O transfer from the excited ozone to allene as the key elementary reaction step.

Excitation of suspensions of ozone and allene in Ar at 250 nm with light from a mercury arc source resulted in the synthesis of the hitherto unobserved molecule $\text{CH}_2=\text{C}=\text{CHOH}$ (propadienol) [107]. The product is explained by direct insertion of $\text{O}(^1\text{D})$, produced by dissociation of $\text{O}_3(^1\text{B}_2)$, into the C-H bond of allene, similar to the synthesis of $\text{CH}_2=\text{CHOH}$ from ethylene and O_3 by Hawkins and Andrews [46].

C. Photochemistry of Molecular Oxygen

Similar to the case of ozone, many photo-induced reactions of organic and inorganic compounds with O_2 have been investigated in cryogenic matrices with the goal of elucidating atmospheric and combustion processes. Most recent studies with molecular oxygen have been reported by Sodeau [108-111], Ault [112-114], and Akimoto [115-119]. Extensive earlier work by Lee [120] has previously been reviewed by Perutz [2]. Reactions investigated by Sodeau and by Ault are typically initiated by UV photodissociation of O_2 or the substrate molecule to yield free O atoms or radical fragments, respectively (in the case of Ault's studies with the output of an excimer laser). Bimolecular reactions of photoexcited polyatomics are not involved, hence a more detailed discussion of these systems lies beyond the topics dealt with in this article.

An intriguing case of excited state bimolecular chemistry are the visible or UV light induced alkene and arene oxidations in solid O_2 reported by Akimoto and coworkers. Suspensions of

small olefins ranging from ethylene to 2,3-dimethyl-2-butene (tetramethylethylene), with all partially CH₃ substituted ethylenes in between [116-118], benzenes, substituted benzene, and of naphthalene [115] in oxygen at 10K revealed well resolved triplet charge transfer absorptions in the near UV or visible spectral region. Absorption tails were found to extend to wavelengths as long as 550 nm (tetramethylethylene). Irradiation of the long wavelength tail of these charge transfer absorptions with narrow band pass filtered light from a high-pressure mercury arc resulted in reaction with O₂ in every case. Typical products were ozone and aldehydes and/or ketones that correspond to oxidative cleavage of the CC double bond. Since the observed reaction thresholds lie below reaction dissociation limits (except for propylene and ethylene), chemistry must occur from bound, non-predissociative levels of the charge transfer state. CO and CO₂ (and HO₂ in the case of C₂H₄ and C₃H₆) were dominant products at short photolysis wavelengths (200-300 nm) that originated in part from secondary photochemistry of initially formed carbonyl compounds. Although contact charge transfer absorptions of unsaturated hydrocarbons and charge transfer state induced chemistry have previously been observed in oxygen saturated liquids and in the vapor phase, as reviewed by Akimoto [115-118], the studies in solid O₂ furnished more precise measurements of the alkene·O₂ charge transfer absorption bands than was previously possible. More importantly, unprecedented insight into the reaction mechanism was gained by trapping of an intermediate in the case of the photooxidation of tetramethylethylene. Therefore, the discussion will focus mainly on the latter reaction.

A single product was obtained upon irradiation of the long wavelength tail of the tetramethylethylene·O₂ charge transfer absorption in the spectral range 400-520 nm [118]. Two oxygen molecules are incorporated in the product according to experiments in matrices ¹⁶O₂:¹⁸O₂ = 1:1, giving rise to a single isotopically mixed modification. This result, and the fact that the vibrational modes attributed to the hydrocarbon moiety were close to those of tetramethylethylene suggest that the observed product is the six-membered ring tetramethyl-1,2,3,4-tetraoxane, shown

in Scheme XII. There is no doubt that the excited charge transfer state is the reactive state because the only conceivable alternative, namely the lowest triplet state of the alkene, would require photolysis wavelengths shorter than 400 nm [116]. Scheme XII shows elementary reaction steps following excitation of the charge transfer state as postulated on the basis of the structure of the trapped tetraoxane. Not surprisingly, photolysis at wavelengths shorter than 400 nm results in multiple products, in part because of secondary photolysis of the tetraoxane intermediate. This underscores the necessity of using narrow band photolysis sources tuned to the long wavelength limit when attempting to trap unstable intermediates.

Loss of product specificity upon photolysis with UV light originates not only from photodissociation of trapped tetraoxane, but in addition from fragmentation of $(\text{CH}_3)_2\text{C}(\text{O}\ddot{\text{O}})-\text{C}(\text{O}\ddot{\text{O}})(\text{CH}_3)_2$ biradical to yield transient dioxymethylene $(\text{CH}_3)_2\text{C}-\text{O}-\ddot{\text{O}}$ (Criegee intermediate). The latter is known to readily fragment to acetone and O atom (to give ozone upon reaction with host O_2 molecules). Although there remains some controversy about the possible involvement of triplet alkene states in the case of photolysis with UV light [116,117], there is little doubt that the lack of trapping of a tetraoxane intermediate in the case of all small olefins but tetramethylethylene has to do with the high photon energies needed to initiate the oxidation. The consequence is that the $\text{RR}'\text{C}(\text{O}\ddot{\text{O}})-\text{C}(\text{O}\ddot{\text{O}})\text{R}''\text{R}'''$ biradical fragments quantitatively. Another example of triplet charge transfer state chemistry may be the photooxidation of a cumulene in O_2 doped solid Ar by 540 nm radiation reported by Sander and Patyk [121].

This example of a reactive charge transfer state adds to the list of reactant excited states unique to cage pairs that can be exploited for controlled bimolecular photochemistry. Other examples involving molecular oxygen are reactions of $\text{O}_2(^1\Delta)$ and $\text{O}_2(^1\Sigma_g^+)$ with organic and

inorganic molecules reviewed previously [11], and photochemistry initiated by O_2 enhanced triplet excitation of the substrate molecule [122,123].

III. HYDROGEN TRANSFER REACTIONS

Photochemical H atom transfer to organic and inorganic substrate molecules in rare gas matrices is one of the standard methods of generating unstable species like HCO, HNO, HO_2 , C_2H_3 etc., as most recently reviewed by Jacox [5] and Perutz [3]. Hydrogen atoms have occasionally been monitored directly, furnishing conclusive evidence for involvement of free H in these cases.

In a recent study of the wavelength dependence of the UV induced HI + acetylene reaction in solid Kr, Abrash and Pimentel discovered that the dynamics may be more subtle in the case of photo-induced H transfer of weak complexes [124,125]. Previous gas phase work by Flygare [126] and infrared matrix work by Andrews [127] had established that weak hydrogen halide-acetylene complexes have a T-shaped structure with the H pointing towards the triple bond. Electronic states relevant to the UV photochemistry of HI are the $1(I)$ and the $O^+(II)$ state, both of which are repulsive as indicated by dashed lines in the potential energy diagram of Fig. 16 [128]. These give rise to a continuous UV absorption with a tail extending to about 320 nm [38].

In an initial set of experiments, irradiation of HI/ $HC\equiv CH$ /Kr matrices with light from a medium-pressure mercury lamp gave vinyl iodide and iodoacetylene as primary (i.e. single photon) products. Photolysis of matrices HI/ $DC\equiv CD$ /Kr and DI/ $HC\equiv CH$ /Kr revealed

isotopic exchange in the acetylene as an additional primary process. Exploiting the diagnostic strengths of infrared monitoring of chemical reactions in rare gas matrices, especially easy differentiation of various isotopically labelled products, separation of isolated reactants and products from those engaged in complexes, and monitoring of the kinetics of reactant depletion and product growth, the authors were able to uncover all elementary photochemical steps involved. Results for the case of $\text{HI} + \text{DC}\equiv\text{CD}$ are displayed in Fig. 17 and Scheme XIII. As can be seen from the $\nu(\text{C-H})$ and $\nu(\text{C-D})$ absorbance growth curves in Fig. 17a and 17b, respectively, there are two distinct isotopic exchange species $\text{HC}\equiv\text{CD}$. One absorbs at 3334 and 2582 cm^{-1} , and exhibits simple first order growth. It is assigned to monodeuteroacetylene produced by reaction of $\text{DC}\equiv\text{CD}$ with free H atoms that originate from photodissociation of isolated HI and diffusion through the matrix. A second set of $\text{HC}\equiv\text{CD}$ modes, absorbing at 3328 , 3326 , and 2577 cm^{-1} , is attributed to $\text{DI}\cdot\text{HC}\equiv\text{CD}$ complexes. As can be seen from Fig. 17, the initial growth of these absorptions indicates that $\text{DI}\cdot\text{HC}\equiv\text{CD}$ is generated by a single photon process, while the decrease upon prolonged irradiation points to subsequent secondary photolysis. Products are $\text{HC}\equiv\text{CI}$ and DCCI according to the sigmoidal shape of their growth curves. An interesting observation is that the $\text{DC}\equiv\text{CI}$ absorbance growth curve (2584 cm^{-1}) shows non-zero slope at the beginning of photolysis while $\text{HC}\equiv\text{CI}$ (3306 cm^{-1}) exhibits zero slope. Hence $\text{HD}\cdot\text{DC}\equiv\text{CI}$ is produced by single photon excitation of $\text{HI}\cdot\text{DC}\equiv\text{CD}$ while $\text{D}_2\cdot\text{HC}\equiv\text{CI}$ is not. This implies that the hydrogen atom of the hydroiodide always ends up in the molecular hydrogen product, a result that allowed Abrash and Pimentel to propose the detailed path for iodoacetylene formation described below. While bands of the various partially deuterated vinyl iodides were too weak to be observed in the $\text{HI} + \text{DC}\equiv\text{CD}$ case, experiments with other isotopic modifications revealed the kinetic behavior of this product. It was found that vinyl iodide undergoes photoelimination of hydrogen iodide to regenerate acetylene and thereby contributes to isotopic exchange in the reactants. Scheme XIII summarizes the observed photochemistry.

Using a Nd:YAG pumped pulsed dye laser equipped with appropriate crystals to generate radiation in the 220-310 nm region, a strong photolysis wavelength dependence of the branching among these products was observed [125]. Irradiation of the weak HI-acetylene complexes at wavelengths longer than 300 nm produced exclusively iodoacetylene, while photolysis at shorter wavelengths gave vinyl iodide, iodoacetylene, and isotope exchanged reactants (Scheme XIV). Recognizing that this photolysis wavelength dependence of the product branching cannot be rationalized simply by assuming reaction of free H atoms with the alkyne, the authors proposed an explanation that is based on electronic state correlations of the $\text{HI} + \text{HC}\equiv\text{CH} \rightarrow \text{I} + \text{C}_2\text{H}_3$ system rather than the $\text{H} + \text{HC}\equiv\text{CH}$ system. Selective access to $1(\text{I})$ and $\text{O}^+(\text{II})$ states by excitation of HI with wavelength tuned light provides a rationale for the observed product distribution. As can be seen from the potential curves and the proposed $\text{HI} + \text{HC}\equiv\text{CH} \rightarrow \text{I} + \text{C}_2\text{H}_3$ state correlations of Fig. 16, and the Franck-Condon envelopes of the corresponding hydrogen iodide transitions [38], the $1(\text{I})$ state of HI is preferentially accessed by photons of wavelengths longer than 300 nm. In this state H transfer leads to $\text{I}(^2\text{P}_{3/2}) + \text{C}_2\text{H}_3(^2\text{A}')$. The latter is vinyl radical in its first electronically excited state [125] (designated by an asterisk in Fig. 16). By contrast, excitation at shorter wavelengths results in access to $\text{HI}(\text{O}^+(\text{II}))$ as well, which couples into $\text{I}(\text{P}_{1/2}) + \text{C}_2\text{H}_3(\tilde{\text{X}}^2\text{A}')$ product states (i.e. excited I atoms and electronic ground state vinyl radical). The two sets of primary transient photoproducts apparently give rise to different continued chemistry, which allows differentiation of $\text{HI}(1(\text{I}))\cdot\text{HC}\equiv\text{CH}$ reaction from $\text{HI}(\text{O}^+(\text{II}))\cdot\text{HC}\equiv\text{CH}$ chemistry. $\text{I}(^2\text{P}_{3/2}) + \text{C}_2\text{H}_3(^2\text{A}')$ yields iodoacetylene and molecular hydrogen as sole products, presumably via α,α -hydrogen elimination from vinyl radical as this would explain why the hydrogen atom originating from the hydrogen iodide always ends up in the hydrogen molecule. $\text{I}(\text{P}_{1/2})$ and $\text{C}_2\text{H}_3(\tilde{\text{X}}^2\text{A}')$, on the other hand, combine to form vinyl iodide or eliminate hydrogen iodide to regenerate HI and acetylene, in the partially deuterated samples under isotopic scrambling. This continued chemistry is indicated in the energy diagram of Fig. 18. The important conclusion drawn from this result is that the chemistry of photo-excited weak $\text{HI}\cdot\text{HC}\equiv\text{CH}$ complexes is controlled by the nature of the $\text{HI} + \text{HC}\equiv\text{CH}$ reactant states, and not merely by the simpler $\text{H} +$

HC≡CH system, despite the fact that both excited states of HI accessed by photo-excitation are dissociative.

The analogy between this H transfer reaction and the large amplitude O transfer of weak $\text{O}_3(^1\text{B}_1)$ complexes (Sect. IIB), and of NO_2 -hydrocarbon collisional pairs (Sect. IIA) is clear. Electronic state correlations of the reactants HI, O_3 , or NO_2 , rather than those of the free atom have to be invoked in order to understand the photolysis wavelength dependence of reaction efficiencies and product branchings despite the fact that free atoms are accessible energetically (except, of course, for NO_2 excited below the dissociation limit). The approximate reaction coordinate for atom transfer is an asymmetric large amplitude stretch in each case. The NO_2 photochemistry constitutes a bridge between a situation in which large amplitude atom transfer is the only accessible transfer coordinate (excitation at wavelengths longer than 398 nm where formation of $\text{O}(^3\text{P})$ is inaccessible) and one in which free atoms can be formed in principle ($\lambda < 398$ nm). In this sense the latter situation is analogous to the ozone and hydrogen iodide case. One would expect the extent to which large amplitude atom transfer can compete with dissociation to free atoms to depend critically on the geometry of the weak complex or collisional pair. In fact, Pimentel stresses the fixed T-shaped geometry of the $\text{HI}\cdot\text{HC}\equiv\text{CH}$ complex as a crucial aspect of the direct coupling of the excited reactants into specific $\text{I} + \text{C}_2\text{H}_3$ product states [125]. By contrast, NO_2 -alkene and NO_2 -alkyne pairs do not give rise to any spectral features that would indicate a preferred, fixed reactant orientation, hence nothing can be said about the geometry of the pairs. However, prolonged photolysis experiments show that reactant pair depletion is essentially quantitative. Therefore, if there were a spread of NO_2 -alkene and NO_2 -alkyne geometries, the implication would be that the relative orientation of the reactants is not critical in the case of the NO_2 systems. This would not be surprising in the light of the fact that reaction is initiated by highly vibrationally excited NO_2 whose amplitudes may be large enough to compensate for unfavorable geometry of the unexcited reactant pairs.

There is an extremely interesting parallel between the photochemistry of weak HI-acetylene complexes in the solid rare gas matrix, and photo-initiated hydrogen transfer of HI and HBr van der Waals complexes with small molecules in a molecular beam [129-131]. The initial idea of photochemistry of weak bimolecular complexes with well defined geometry in a beam, proposed by Wittig [129, 130], was to study H atom reactions under conditions with restricted collision parameters. The results of recent work clearly show that the dynamics of the excited hydrogen halide molecule itself dictates the observed product state distributions, similar to the conclusion arrived at in the matrix study of the HI-acetylene system [125]. Very fruitful interaction can be expected in the future between such precursor geometry limited photochemistry of van der Waals complexes in molecular beams, and corresponding studies on collisional pairs and weak complexes in inert solid matrices. This includes state-specific metal atom-molecule reactions pioneered by Soep and collaborators [132].

IV. CONCLUDING REMARKS

The recent work on wavelength selective photochemistry of collisional pairs and weak complexes in cryogenic matrices reviewed in this article illustrates the unique contribution this technique is able to make to our understanding of bimolecular reactions paths. Photooxidations of unsaturated hydrocarbons by nitrogen dioxide show how NO trapping of transient biradicals in their nascent structure, including conformation, can be used to gain new insight into the regio- and stereochemistry of oxygen transfer to CC double and triple bonds. In some cases, electronic hypersurfaces accessed upon reaction can be inferred from the structure of the trapped transients. Most revealing are reactions that exhibit hypersurface-dependent product branchings, with the

electronic state dependent photochemistry of weak ozone and HI complexes as particularly intriguing examples since reaction occurs from (pre)dissociative states. Of course, such progress would have been impossible without laser sources which are continuously tunable throughout the UV, visible, and the near infrared regions. The results discussed here are intended to encourage the routine use of these tools in matrix photochemical experiments.

Beyond mechanistic insight that is specific to each system discussed, the most significant advance in the work reviewed here is the recognition of the role of large amplitude atom transfer. There is mounting evidence that reaction efficiencies and product branchings are controlled by the direct coupling of excited reactant states into product states by large amplitude atom transfer even upon excitation above dissociation thresholds, as shown by the photochemistry of ozone and HI complexes. This mechanism may well be one of the main reasons why many bimolecular reactions in matrices are limited to cage pairs even if formation of free atoms by photodissociation of isolated reactants is energetically accessible. Moreover, it cautions against the assumption that free atom chemistry is involved every time atom transfer is initiated in a matrix by photodissociation of a precursor molecule. Clearly, the understanding of the mechanistic and dynamical aspects of bimolecular photochemistry in solid matrices would greatly benefit from a better knowledge of reactant pair geometries, particularly in those cases where no complexes are formed.

A very exciting aspect of wavelength controlled photochemistry of collisional pairs and weak complexes in solid matrices is the special opportunity it offers in terms of product specific synthesis. Several different types of excited states unique to reactant pairs that can be exploited for controlled chemistry have been discussed in this review, and there is no doubt that more will be discovered as new systems are explored.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76-SF00098. I thank Ms. Jennifer Knox for preparing the typescript.

REFERENCES

1. G.C. Pimentel, in Formation and Trapping of Free Radicals, (A.M. Bass and H.P. Broida, eds.), Academic Press, New York, 1960.
2. R.N. Perutz, in Chemistry and Physics of Matrix-Isolated Species, (L. Andrews and M. Moskovits, eds.), North-Holland, Amsterdam, 1989.
3. R.N. Perutz, Chem. Rev., **85**, 77 (1985).
4. R.N. Perutz, Chem. Rev., **85**, 97 (1985).
5. M.E. Jacox, in Chemistry and Physics of Matrix-Isolated Species, (L. Andrews and M. Moskovits, eds.), North-Holland, Amsterdam, 1989.
6. I.R. Dunkin, in Chemistry and Physics of Matrix-Isolated Species, (L. Andrews and M. Moskovits, eds.), North-Holland, Amsterdam, 1989.
7. R. H. Hauge, J.L. Margrave, and Z.H. Kafafi, in Chemistry and Physics of Matrix-Isolated Species, (L. Andrews and M. Moskovits, eds.), North-Holland, Amsterdam, 1989.
8. M.J. Almond and A.J. Downs, in Advances in Spectroscopy, Vol. 17, (R.J.H. Clark and R.E. Hester, eds.), Wiley, New York, 1989.
9. M. Poliakoff and J.J. Turner, in Chemical and Biochemical Applications of Lasers, Vol. 5, (C.B. Moore, ed.), Academic Press, New York, 1980.
10. H. Frei and G.C. Pimentel, Ann. Rev. Phys. Chem., **36**, 491 (1985).
11. H. Frei and G.C. Pimentel, in Chemistry and Physics of Matrix-Isolated Species (L. Andrews and M. Moskovits, eds.) North-Holland, Amsterdam, 1989.
12. M. A. Young and G.C. Pimentel, J. Appl. Opt., **28**, 4270 (1989).
13. H. Hamaguchi, in Vibrational Spectra and Structure, Vol. 16, (J.R. Durig ed.), Elsevier, Amsterdam, 1987.
14. N.J. Turro, Pure Appl. Chem., **58**, 1219 (1986).
15. L. Andrews and M. Moskovits, in Chemistry and Physics of Matrix-Isolated Species, (L. Andrews and M. Moskovits, eds.), North-Holland, Amsterdam, 1989.
16. D.J. Hucknall, Chemistry of Hydrocarbon Combustion, Chapman and Hall, London, 1985.
17. R.P. Wayne, Chemistry of Atmospheres, Oxford University Press, Oxford, 1991.
18. H.H. Szmant, Organic Building Blocks of the Chemical Industry, Wiley, New York, 1989.
19. M. Nogradi, Stereoselective Synthesis, VCH Verlagsgesellschaft, Weinheim, 1987.
20. M. Nakata and H. Frei, J. Am. Chem. Soc., **111**, 5240 (1989).

21. M. Nakata and H. Frei, J. Phys. Chem., **93**, 7670 (1989).
22. H. Frei, Chimia, **45**, 175 (1991).
23. H. Kuehne, M. Forster, J. Hulliger, H. Ruprecht, A. Bauder, and H.H. Günthard, Helv. Chim. Acta, **63**, 1971 (1980).
24. P. Tarte, J. Chem. Phys., **20**, 1570 (1952).
25. A.J. Barnes, H.E. Hallam, S. Waring, and J.R. Armstrong, J. Chem. Soc. Faraday Trans. 2, **72**, 1 (1976).
26. B.J. van der Veken, R. Maas, G.A. Guirgis, H.D. Stidham, T.G. Sheehan, and J.R. Durig, J. Phys. Chem., **94**, 4029 (1990).
27. P.N. Gosh and H.H. Günthard, Spectrochim. Acta, Part A, **37**, 1055 (1981).
28. A.J. Barnes, in Matrix Isolation Spectroscopy, (A.J. Barnes, ed.), Reidel, Dordrecht, 1981, p. 531.
29. G. Berti, Topics in Stereochemistry, Vol. 7, (E.L. Eliel and N.L. Allinger, eds.), 1973, p. 93.
30. P.C. Bartlett, Rec. Chem. Prog., **18**, 111 (1957).
31. R.P. Hanzlik and G.O. Shearer, J. Am. Chem. Soc., **97**, 5231 (1975).
32. D.J. Fitzmaurice and H. Frei, to be submitted.
33. M. Dupuis, J.J. Wendoloski, T. Takada, and W.A. Lester, Jr., J. Chem. Phys., **76**, 481 (1982).
34. T. Fueno, Y. Takahara, and K. Yamaguchi, Chem. Phys. Lett., **167**, 291 (1990).
35. C.F. Melius, quoted in reference [36].
36. A.M. Schmoltner, P.M. Chu, and Y.T. Lee, J. Chem. Phys., **91**, 5365 (1989).
37. M. Nakata, K. Shibuya, and H. Frei, J. Phys. Chem., **94**, 8168 (1990).
38. H. Okabe, Photochemistry of Small Molecules, Wiley, New York, 1978.
39. D.K. Hsu, D.L. Monts, and R.N. Zare, Spectral Atlas of Nitrogen Dioxide, Academic Press, New York, 1978.
40. R.E. Smalley, L. Wharton, and D.H. Levy, J. Chem. Phys., **63**, 4977 (1975).
41. D.J. Fitzmaurice and H. Frei, to be submitted.
42. R.J. Cvetanovic and D.L. Singleton, Rev. Chem. Intermed., **5**, 183 (1984).
43. Y. Endo, S. Tsuchiya, C. Yamada, E. Hirota, and S. Koda, J. Chem. Phys., **85**, 4446 (1986).

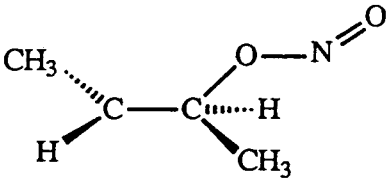
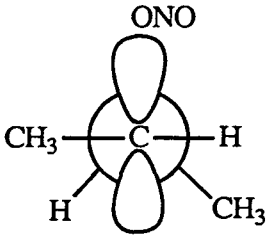
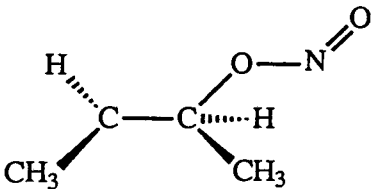
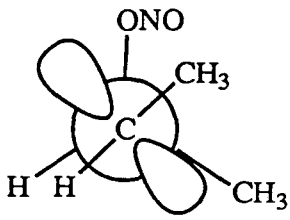
44. A. M. Schmoltner, P.M. Chu, R.J. Brudzynski, and Y.T. Lee, J. Chem. Phys. **91**, 6926 (1989).
45. R.A.Y. Jones, Physical and Mechanistic Organic Chemistry, Cambridge University Press, Cambridge, 1987, p. 131.
46. M. Hawkins and L. Andrews, J. Am. Chem. Soc., **105**, 2523 (1983).
47. R. Atkinson, S.M. Aschmann, A.M. Winer, and J.N. Pitts, Jr., Int. J. Chem. Kinet., **16**, 697 (1984).
48. T. Ohta, H. Nagura, and S. Suzuki, Int. J. Chem. Kinet., **18**, 1 (1986).
49. H. Shechter, Rec. Chem. Prog., **25**, 55 (1964).
50. D.H. Giamalva, G.B. Kenion, D.F. Church, and W.A. Pryor, J. Am. Chem. Soc. **109**, 7059 (1987).
51. M. Nakata and H. Frei, J. Chem. Soc. Jpn., 1412 (1989).
52. D.J. Fitzmaurice and H. Frei, J. Phys. Chem. **95**, 2652 (1991).
53. R.A. Pickering and C.C. Price, J. Am. Chem. Soc., **80**, 4931 (1958).
54. M. Hanack, Conformational Theory, Academic Press, New York, 1965, p. 98.
55. G.N. Zhizhin and Kh. E. Sterin, in Vibrational Spectra and Structure, Vol. 9, (J.R. Durig, ed.), Marcel Dekker, New York, 1981, p. 242.
56. J.L. Offenbach, L. Fredin, and H.L. Strauss, J. Am. Chem. Soc., **103**, 1001 (1981).
57. Y. Hori, S. Shimada, and H. Kashiwabara, J. Phys. Chem., **90**, 3073 (1986).
58. M.R. Imam and N.L. Allinger, J. Mol. Struct., **126**, 345 (1985).
59. D.H. Wertz and N.L. Allinger, Tetrahedron, **30**, 1579 (1974).
60. W.A. Lester, Jr., M. Dupuis, T.J. O'Donnell, and A.J. Olsen, in Frontiers in Chemistry, (K.J. Laidler, ed.), Pergamon Press, New York, 1982, p. 159.
61. M. Nakata and H. Frei, J. Am. Chem. Soc., **114**, 000 (1992).
62. K. A. Singmaster and G.C. Pimentel, J. Mol. Struct., **194**, 215 (1989).
63. G. Maier, H.P. Reisenauer, B. Rohde, and K. Dehnike, Chem. Ber., **116**, 732 (1983).
64. B.L. Hammond, S.Y. Huang, and W.A. Lester, Jr., J. Phys. Chem., **94**, 7969 (1990).
65. Y. Osamura, W.T. Borden, and K. Morokuma, J. Am. Chem. Soc. **106**, 5112 (1984).
66. L. Salem, Electrons in Chemical Reactions: First Principles, Wiley, New York, 1982.
67. A.M. Schmoltner, S.Y. Huang, R.J. Brudzynski, P.M. Chu, and Y.T. Lee, submitted.

68. W.H. Fletcher and W.B. Barish, Spectrochim. Acta, **21**, 1647 (1965).
69. R. Hochstrasser and J. Wirz, Angew. Chem. Int. Ed. Engl., **29**, 411 (1990).
70. F. Debu, M. Monnier, P. Verlaque, G. Davidovics, J. Pourcin, H. Bodot, and J. P Aycard, C.R. Acad. Sci. Paris Ser. 2, **303**, 897 (1986).
71. J.R. Durig, S.E. Hannum, and S.C. Brown, J. Phys. Chem., **75**, 1946 (1971).
72. J. Hamer and A. Macaluso, Chem. Rev., **64**, 473 (1964).
73. B.C. Gilbert and W.M. Gulick, Jr. J. Phys. Chem., **73**, 2448 (1969).
74. J. A. Harrison and H. Frei, to be submitted.
75. J.A. Berson, Acc. Chem. Res., **11**, 466 (1978).
76. L.B. Harding and A.F. Wagner, J. Phys. Chem., **90**, 2974 (1986).
77. J. Bargon, K. Tanaka, and M. Yoshimine, in Computational Methods in Chemistry, (J. Bargon, ed.), Plenum, New York, 1980, p. 239.
78. K. Tanaka and M. Yoshimine, J. Am. Chem. Soc., **102**, 7655 (1980).
79. C. Bachmann, T.Y. N'Guessan, F. Debu, M. Monnier, J. Pourcin, J.-P. Aycard, and H. Bodot, J. Am. Chem. Soc., **112**, 7488 (1990).
80. W.J. Bouma, R.H. Nobes., L. Radom, and C.E. Woodward, J. Org. Chem., **47**, 1869 (1982).
81. G. Vacek, B.T. Colegrove, and H.F. Schaeffer, Chem. Phys. Lett., **177**, 468 (1991).
82. E.G. Lewars, Chem. Rev., **83**, 520 (1983).
83. M. Torres, E.M. Lown, H.E. Gunning, and O.P. Strausz, Pure and Appl. Chem., **52**, 1623 (1980).
84. H. Hollenstein and H.H. Günthard, Spectrochim. Acta, Part A, **27**, 2027 (1971).
85. A.M. Schmoltner, P.M. Chu, and Y.T. Lee, J. Chem. Phys., **91**, 5365 (1989).
86. A.K. Biswas, The Ozone Layer, Pergamon Press, New York, 1979.
87. P.S. Bailey, Ozonation in Organic Chemistry, Academic Press, New York, 1978.
88. H. Kuehne, S. Vaccani, A. Bauder, and H.H. Günthard, Chem. Phys., **28**, 11 (1978).
89. F.J. Racoczi, T.K. Ha, and H.H. Günthard, Chem. Phys., **74**, 273 (1983).
90. C.K. Kohlmiller and L. Andrews, J. Am. Chem. Soc., **103**, 2578 (1981).
91. M.Hawkins, C.K. Kohlmiller, and L. Andrews, J. Phys. Chem., **86**, 3154 (1982).
92. L. Andrews and C.K. Kohlmiller, J. Phys. Chem., **86**, 4548 (1982).

93. B. Nelander and L. Nord, Tetrahedron Lett., 2821 (1977).
94. P. J. Hay, R.T. Pack, R.B. Walker, and E.J. Heller, J. Phys. Chem., **86**, 862 (1982).
95. K.H. Thunemann, S.D. Peyerimhoff, and R.J. Buenker, J. Mol. Spectrosc., **70**, 432 (1978).
96. P.J. Hay and T.H. Dunnig, J. Chem. Phys., **67**, 2290 (1977).
97. H.B. Levene, J.C. Nieh, and J.J. Valentini, J. Chem. Phys., **87**, 2583 (1987).
98. R. Withnall, M. Hawkins, and L. Andrews, J. Phys. Chem., **90**, 575 (1986).
99. R. Withnall and L. Andrews, J. Phys. Chem., **91**, 784 (1987).
100. L. Andrews, R. Withnall, and B.W. Moores, J. Phys. Chem., **93**, 1279 (1989).
101. L. Andrews and R. Withnall, J. Am. Chem. Soc., **110**, 5605 (1988).
102. B.W. Moores and L. Andrews, J. Phys. Chem., **93**, 1902 (1989).
103. L. Andrews, B.W. Moores, and K.K. Fonda, Inorg. Chem., **28**, 290 (1989).
104. R. Withnall and L. Andrews, J. Phys. Chem., **94**, 2351 (1990).
105. L. Andrews, in Chemistry and Physics of Matrix Isolated Species, (L. Andrews and M. Moskovits, eds.), North-Holland, Amsterdam, 1989.
106. L. Andrews, in Vibrational Spectra and Structure, Vol. 18, (J.R. Durig, ed.), Elsevier, Amsterdam, 1990.
107. K.A. Singmaster and G.C. Pimentel, J. Mol. Struct., **200**, 225 (1989).
108. J.R. Sodeau, A. Beeby, and L.J. Whyte, Spectrochim. Acta, Part A, **46**, 887 (1990).
109. K.C. Clemitshaw and J.R. Sodeau, J. Phys. Chem., **93**, 3552 (1989).
110. J. N. Crowley and J.R. Sodeau, J. Phys. Chem., **93**, 4785 (1989).
111. K.C. Clemitshaw and J.R. Sodeau, J. Phys. Chem., **91**, 3650 (1987).
112. J. L. Laboy and B.S. Ault, J. Photochem. Photobiol., Part A, **59**, 19 (1991).
113. B.S. Ault, J. Mol. Struct., **222**, 1 (1990).
114. B.S. Ault, J. Phys. Chem., **93**, 2456 (1989).
115. S. Hashimoto and H. Akimoto, J. Phys. Chem., **93**, 571 (1989).
116. S. Hashimoto and H. Akimoto, J. Phys. Chem., **91**, 1347 (1987). See Also R.I. Martinez [117].
117. R.I. Martinez, J. Phys. Chem., **91**, 1345 (1987).

118. S. Hashimoto and H. Akimoto, J. Phys. Chem., **90**, 529 (1986).
119. H. Bandow and H. Akimoto, J. Phys. Chem., **89**, 845 (1985).
120. M. Green and E.K.C. Lee, J. Phys. Chem., **90**, 6470 (1986).
121. W. Sander and A. Patyk, Angew. Chem., **99**, 495 (1987).
122. H. Frei, J. Chem. Phys., **80**, 5616 (1984).
123. M. McCluskey and L. Andrews, J. Phys. Chem., **95**, 2679 (1991).
124. S.A. Abrash and G.C. Pimentel, J. Phys. Chem., **93**, 5828 (1989).
125. S.A. Abrash and G.C. Pimentel, J. Phys. Chem., **93**, 5834 (1989).
126. A.C. Legon, P.D. Aldrich, and W.H. Flygare, J. Chem. Phys., **75**, 625 (1981).
127. L. Andrews, G.L. Johnson, and B.J. Kelsall, J. Phys. Chem., **86**, 3374 (1982).
128. D.A. Chapman, K. Balasubramanian, and S.H. Lin, J. Chem. Phys., **87**, 5325 (1987).
129. S.K. Shin, Y. Chen, S. Nickolaissen, S.W. Sharpe, R.A. Beaudet, and C. Wittig, Adv. Photochem., **16**, 249 (1991).
130. C. Wittig, S. Sharpe, and R.A. Beaudet, Acc. Chem. Res., **21**, 341 (1988).
131. M. Takayanagi and I. Hanazaki, Chem. Rev., **91**, 1193 (1991).
132. M.C. Duval, B. Soep, and W.H. Breckenridge, J. Phys. Chem., **95**, 7145 (1991).

TABLE 1:
Infrared Spectra of 2-Butyl Nitrite Radicals in Matrices
2-Butene/ NO_2 /Ar = 2.5/1/400

Frequency, cm^{-1}				Assignment
$\text{C}_4\text{H}_8\text{ONO}$	$\text{C}_4\text{H}_8^{16}\text{ON}^{18}\text{O}$	$\text{C}_4\text{H}_8^{18}\text{ON}^{16}\text{O}$	$\text{C}_4\text{H}_8^{18}\text{ON}^{18}\text{O}$	
 I_t 				
1645.5 (0.90) ^a	1605.0	1644.2	1605.0	$\nu(\text{N}=\text{O})$
1366.7 (0.06)	1366.7	1366.7	1366.7	$\delta(\text{CH}_3)$
1035.0 (0.04)	1033.4	1031.8	1030.3	$\nu(\text{C}-\text{C})$
920.5 (0.08)	914.9	906.9	901.2	$\nu(\text{C}-\text{O})$
754.6 (1.00)	754.6	735.8	735.8	$\nu(\text{O}-\text{N})$
 I_c 				
1652.0 (1.00)			1610.0	$\nu(\text{N}=\text{O})$
1373.5 (0.08)			1373.6	$\delta(\text{CH}_3)$
1051.6 (0.03)			1047.0	$\nu(\text{C}-\text{C})$
986.8 (0.06)			981.2	$\nu(\text{C}-\text{C})$
837.4 (0.23)			834.4	$\nu(\text{C}-\text{C})$
771.9 (1.00)			755.0	$\nu(\text{O}-\text{N})$
651.2 (0.09)			639.7	$\delta(\text{CCO})$

^a relative absorbance

TABLE 2

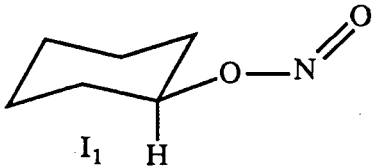
Ethylene + NO₂: Photolysis Wavelength Dependence of Reaction Quantum Efficiency

λ_{phot}	$\phi_t(\lambda)/\phi_t(574 \text{ nm})$	$k_{3a}/(k_1 + k_{3a}) = \text{Acetaldehyde Yield}$
574 nm	(1.0)	0
555	7.7	0.14
543	9.0	0.38
514	13.4	0.35
488	12.7	0.31

Table 3:

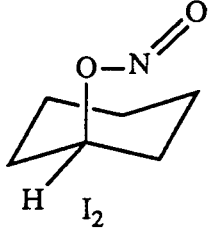
Infrared Spectra of Cyclohexyl Nitrite Radicals in Matrices
Cyclohexene/NO₂/Ar = 2.5/1/100

Frequency, cm ⁻¹			Assignment
C ₆ H ₁₀ ONO	C ₆ H ₁₀ ¹⁸ ON ¹⁸ O	C ₆ H ₁₀ O ¹⁵ NO	



I₁

1655 (1.03) ^a	1613	1627	ν(N=O)
1452 (0.12)	1452	1452	δ(CH ₂)
1376 (0.06)	1376	1376	δ(CH ₂)
1050 (0.08)	1039	1049	ν(C-O)
837 (0.35)	835	836	γ _r (CH ₂)
808 (0.23)	807	807	γ _r (CH ₂)
769 (1.00)	760	762	ν(O-N)
675 (0.28)	653	672	δ(CCO)

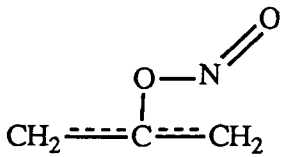


I₂

1644 (1.18) ^a	1604	1616	ν(N=O)
1430 (0.05)	1430	1430	δ(CH ₂)
1167 (0.06)	1165	1165	γ _w (CH ₂)
1102 (0.03)	---	---	ν(C-C)
1010 (0.04)	1010	1007	
960 (0.11)	940	954	ν(C-O)
819 (0.18)	818	819	γ _r (CH ₂)
756 (1.00)	735	746	ν(O-N)

^a absorbance normalized to that of the ν(O-N) band.

TABLE 4:
Infrared Spectrum of Allyl Nitrite Radical in an Allene/ $\text{NO}_2/\text{Ar} = 2.5/1/200$ Matrix

Frequency, cm^{-1}		
$\text{C}_3\text{H}_4\text{ONO}$	$\text{C}_3\text{H}_4\text{O}^{15}\text{NO}$	$\text{C}_3\text{D}_4\text{ONO}$
		
1673.7 (1.00) ^a	1644.5	1673.7
1429.0 (0.03)	1429.0	1116.6
1370.6 (0.14)	1370.5	1014.5
1334.8 (0.08)	1334.1	995.0
1023.6 b	1021.0	908.0
957.7 (0.06)	956.1	844.6
862.8 (0.45)	862.8	838.9
765.7 (1.18)	755.7	742.6
605.0 (0.29)	602.0	685.0

^a Relative absorbance

^b Band overlaps with allene absorption.

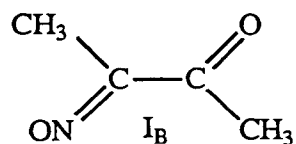
TABLE 5:

Infrared Spectra of Acetyl Methyl Iminoxy Radical in a Matrix
 Dimethylacetylene/NO₂/Ar = 2.5/1/200

Frequency, cm ⁻¹			Assignment ^c
C ₄ H ₆ O ₂ N	C ₄ H ₆ O ₂ ¹⁵ N	C ₄ H ₆ ¹⁸ O ₂ N	

I_A

1707.0 (1.08) ^a	1705.4	1677	v(C=O)
1560.3 (1.00)	1532.2	1546	} v(C=N)
1545.3 (0.10)	1523.9	1534	
1425.6 (0.31)	1424.0	---	δ(CH ₃) _{as}
1394.6 (0.11)	1392.8	1391	δ(CH ₃) _{as}
1392.4 (0.11)			
1360.3 (0.32)	1359.6	1359	δ(CH ₃) _s
1333.2 (0.50)	1328.8	1332	} γ _r (CH ₃), v(N-O)
1258.0 (0.47)	1258.0	---	
1239.6 (0.12)	1232.0	1239	
1130.8 (0.52)	1128.5	1128	v(C-CH ₃) _{as}
1003.6 (0.09)	1003.2	1003	} v(C-C), γ _r (CH ₃)
977.4 (0.12)	972.7	975	
958.8 (0.36)	958.4	955	
692.8 (0.15)	689.4	693	v(C-CH ₃) _s
621.6 (0.38)	617.4	616	δ(CCO)

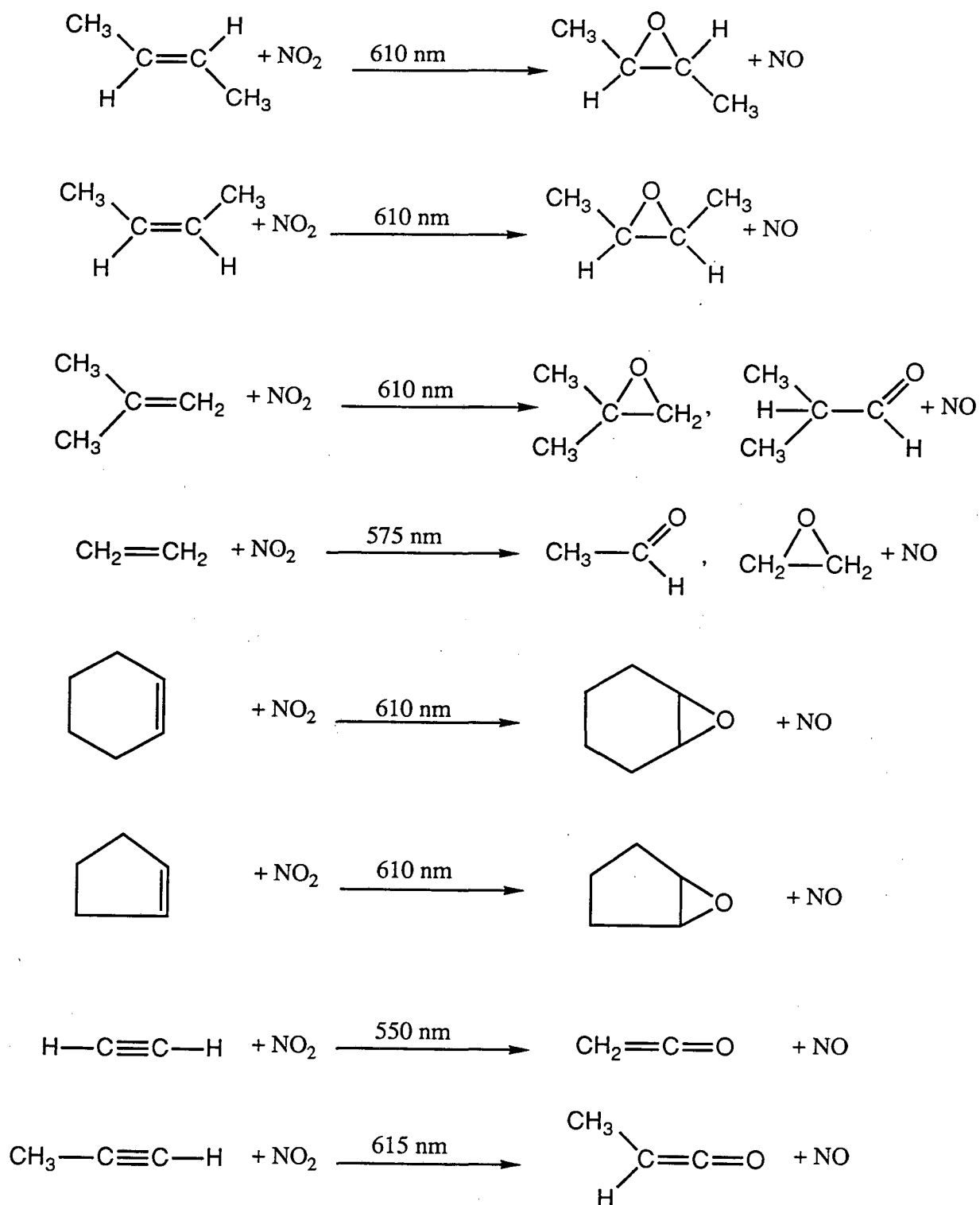


1716.7 (0.56)	1715.3	1684	I _{B1}	}	v(C=O)
1711.2 (0.34)	1708.8	1681	I _{B2}		
(1600) ^b	^b	(1590) ^b	I _{B1}	}	v(C=N)
1591.4 (0.31)	(1566.6) ^b	^b	I _{B2}		
1436.8 (0.05)	1436.8	---	I _{B2}	}	δ(CH ₃) _{as}
1429.7 (0.06)	1429.2	---	I _{B2}		
1399.3 (0.06)	1399.7	---	I _{B1}	}	δ(CH ₃) _{as}
1389.1 (0.04)	1389.1	---	I _{B2}		
1375.1 (0.42)	1374.4	1374	I _{B1}	}	δ(CH ₃) _{as}
1372.7 (0.14)	1372.0	---	I _{B2}		
1368.6 (0.31)	1368.3	1368	I _{B2}	}	γ _r (CH ₃), v(N-O)
1363.4 (0.22)	1363.3	1363	I _{B1}		
1335.6 (0.15)	1333.3	1335	I _{B2}	}	v(C-CH ₃) _{as}
1328.7 (0.04)	1327.2	1325	I _{B1}		
1301.0 (1.00)	1294.9	---	I _{B2}	}	v(C-CH ₃) _{as}
1261.2 (1.00)	1256.7	---	I _{B1}		
1119.7 (0.31)	1120.3	1120	I _{B2}	}	v(C-CH ₃) _{as}
1116.1 (0.21)	1115.8	1116	I _{B1}		
993.4 (0.05)	994.0	994	I _{B2}	}	v(C-C), γ _r (CH ₃)
986.5 (0.10)	984.3	982	I _{B1}		
963.4 (0.17)	963.2	956	I _{B2}	}	δ(CCO)
953.0 (0.07)	952.7	945	I _{B1}		
608.3 (0.25)	606.2	598	I _{B2}	}	δ(CCO)
602.5 (0.15)	600.7	593	I _{B1}		
598.4 (0.16)	594.7	587	I _{B2}		
590.9 (0.07)	590.4	585			

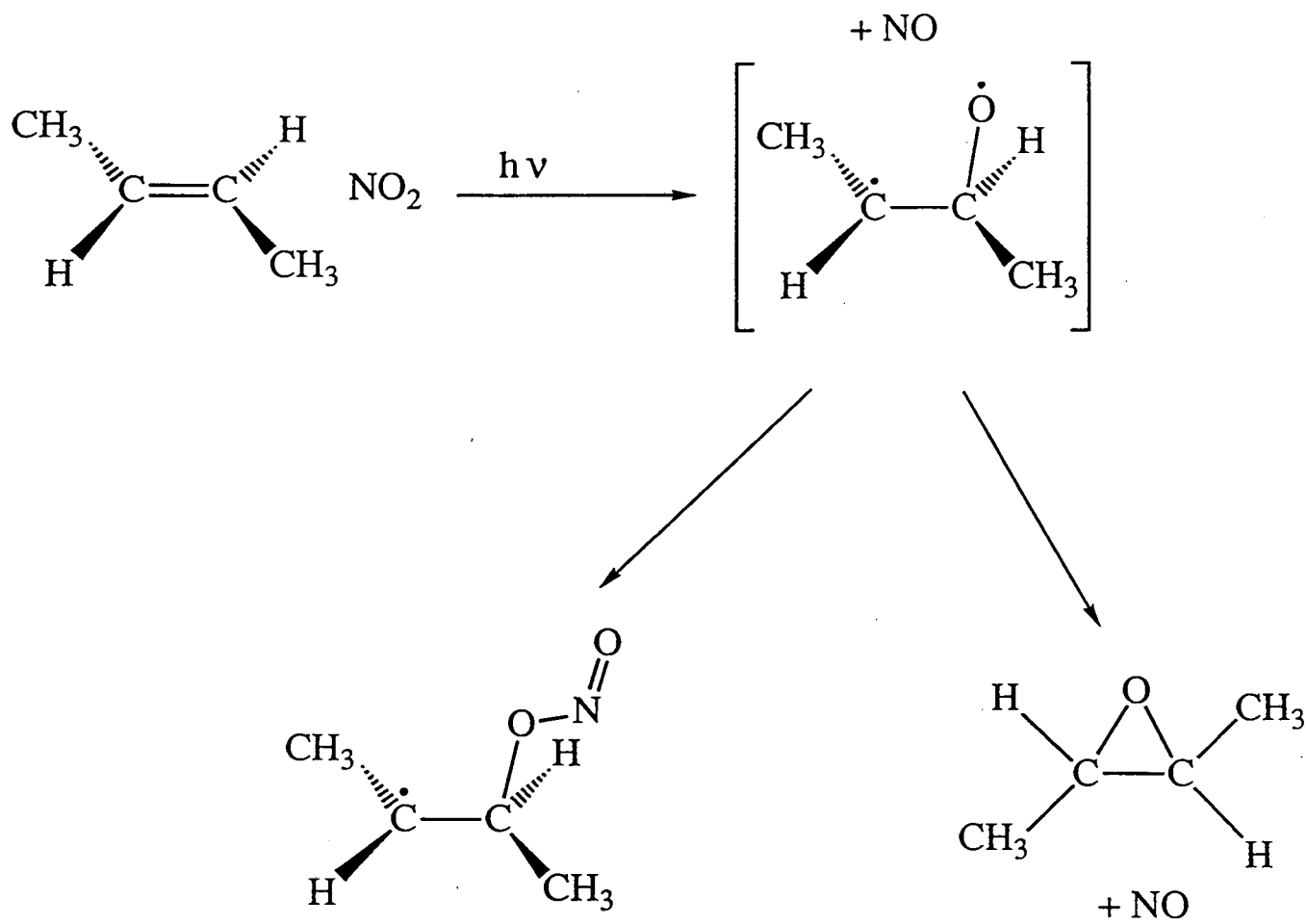
^a Relative absorbance.

^b Band overlapped by NO₂ absorption.

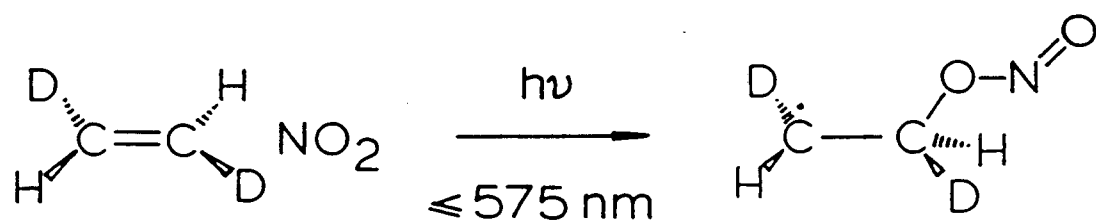
^c Empirical mode assignment based in part on the vibrational spectrum of biacetyl [71].



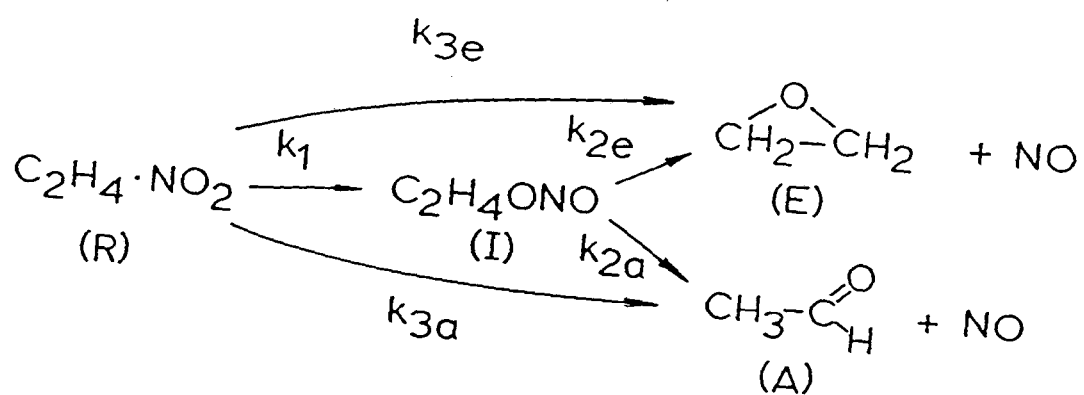
Scheme I



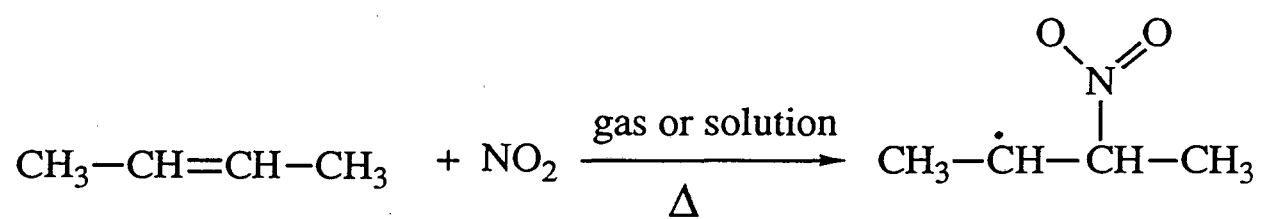
Scheme II



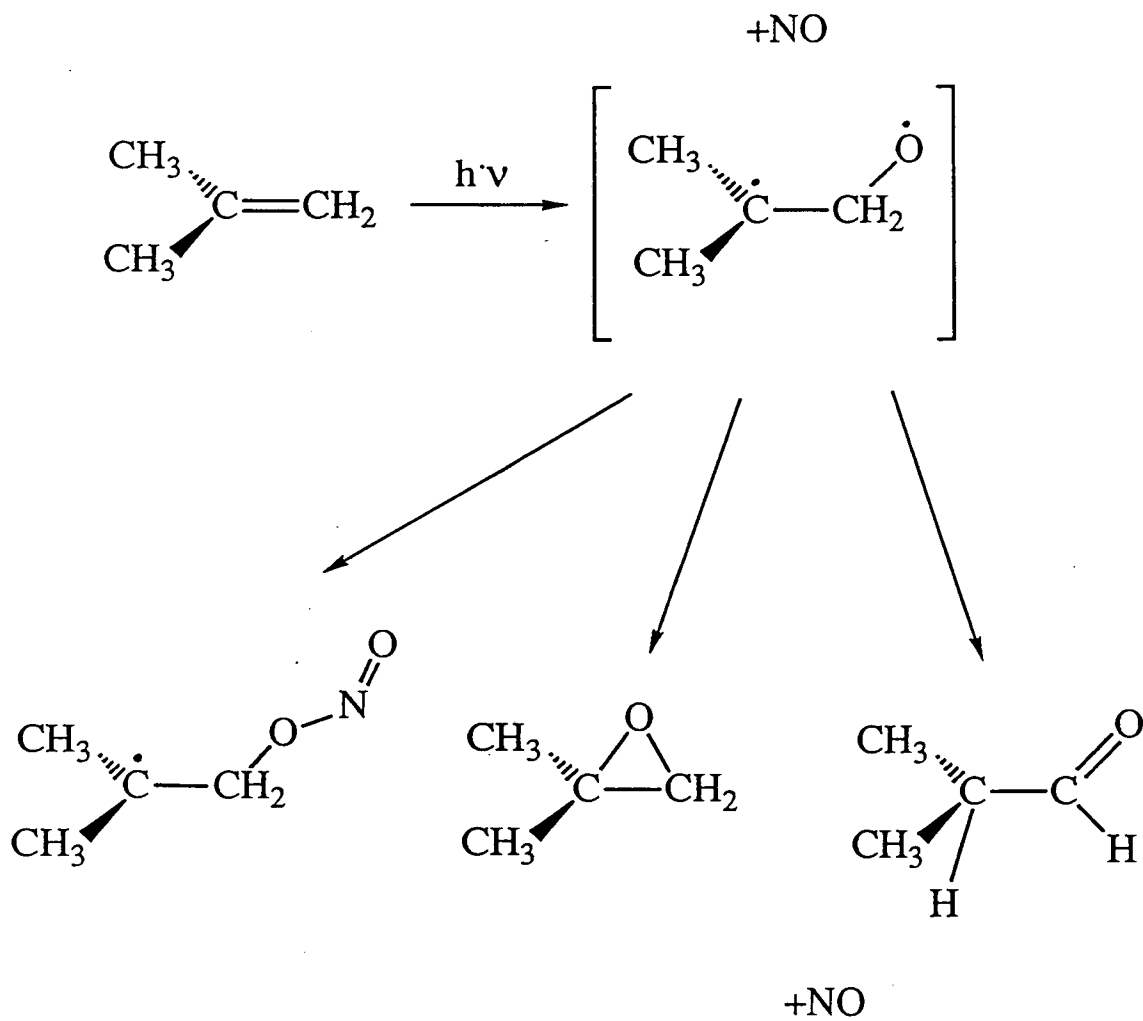
Scheme III



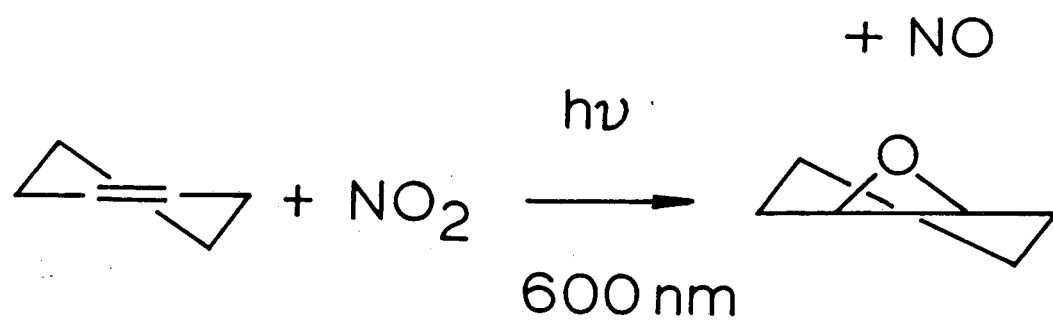
Scheme IV



Scheme V

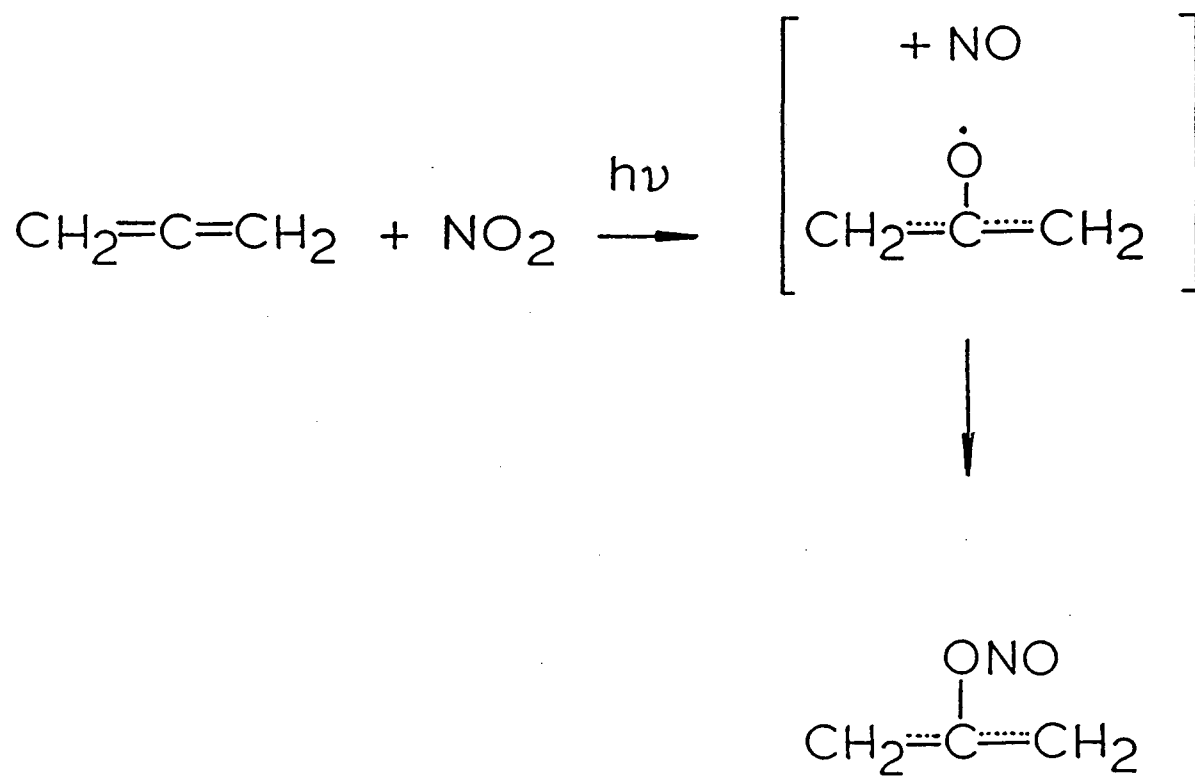


Scheme VI

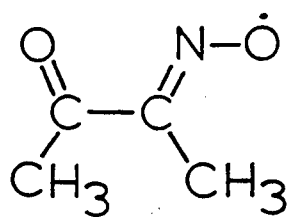


XBL 912-293

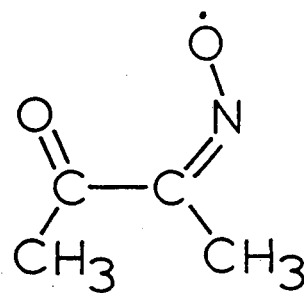
Scheme VII



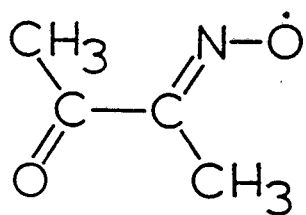
Scheme VIII



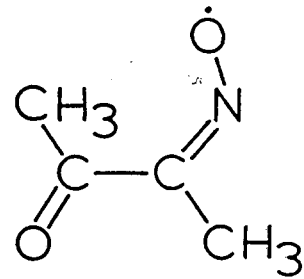
s-cis trans



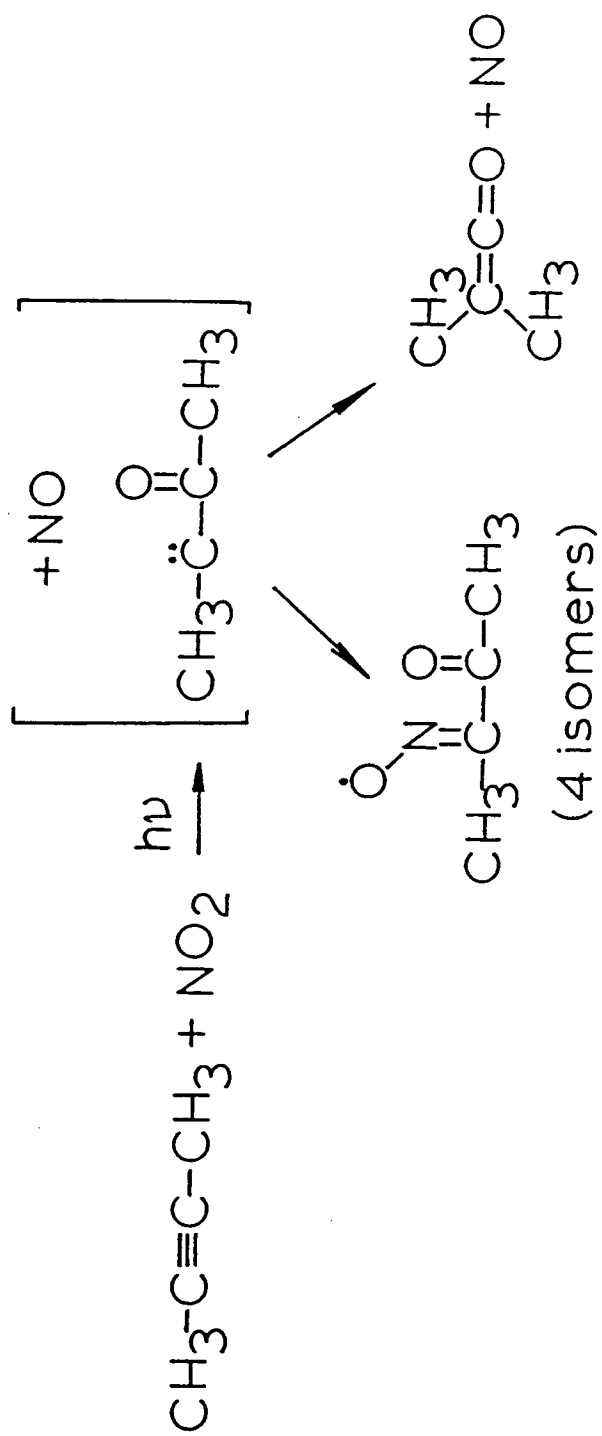
s-cis cis



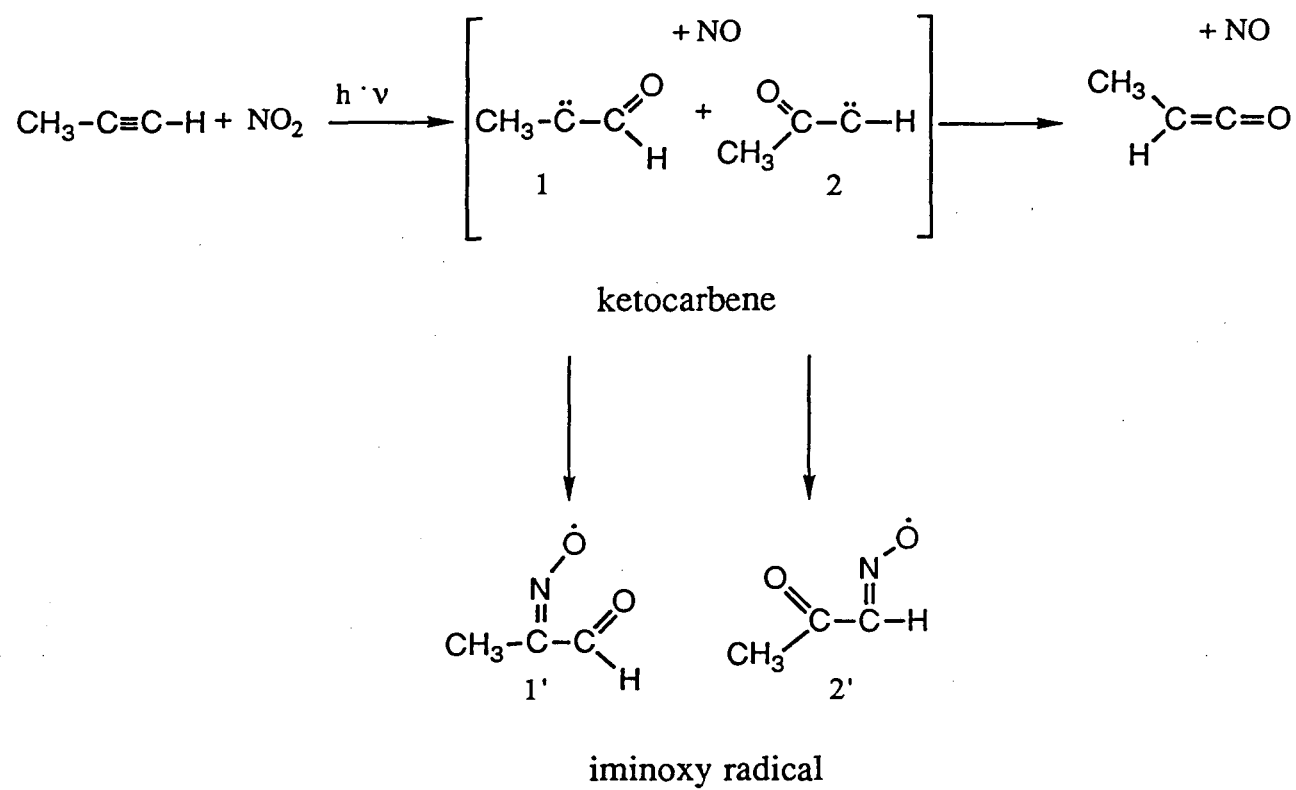
s-trans trans



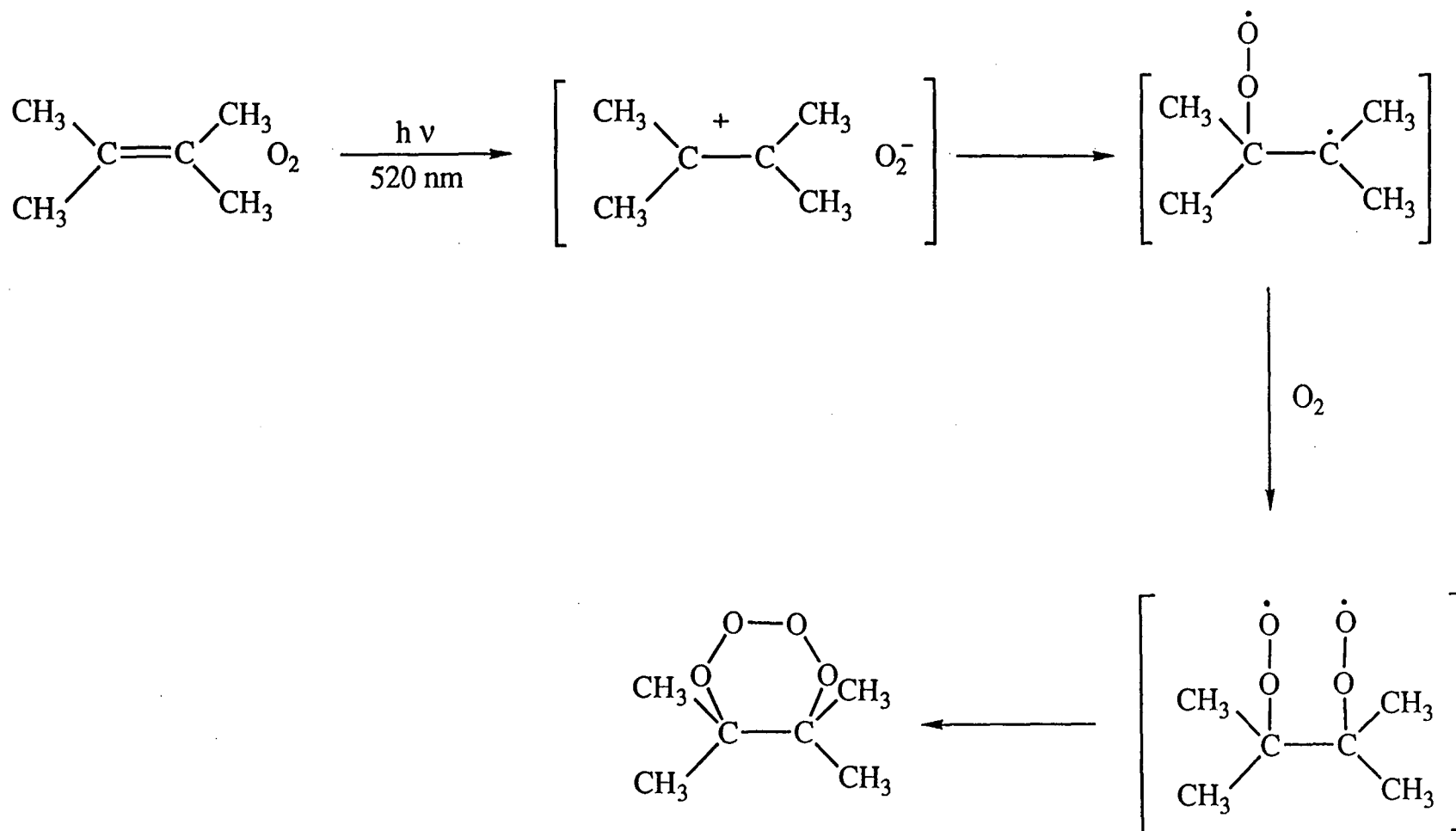
s-trans cis



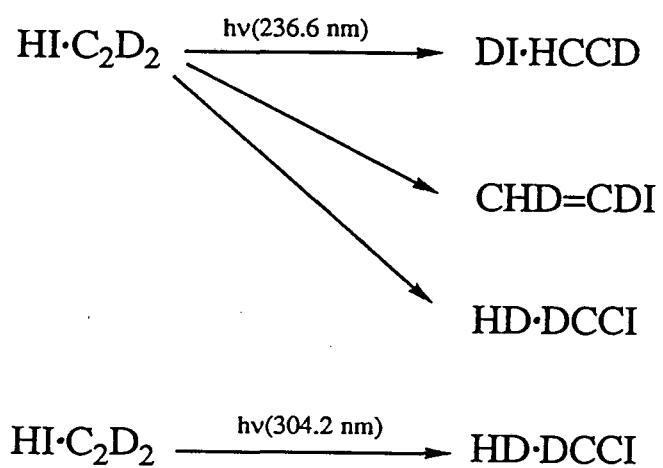
Scheme X



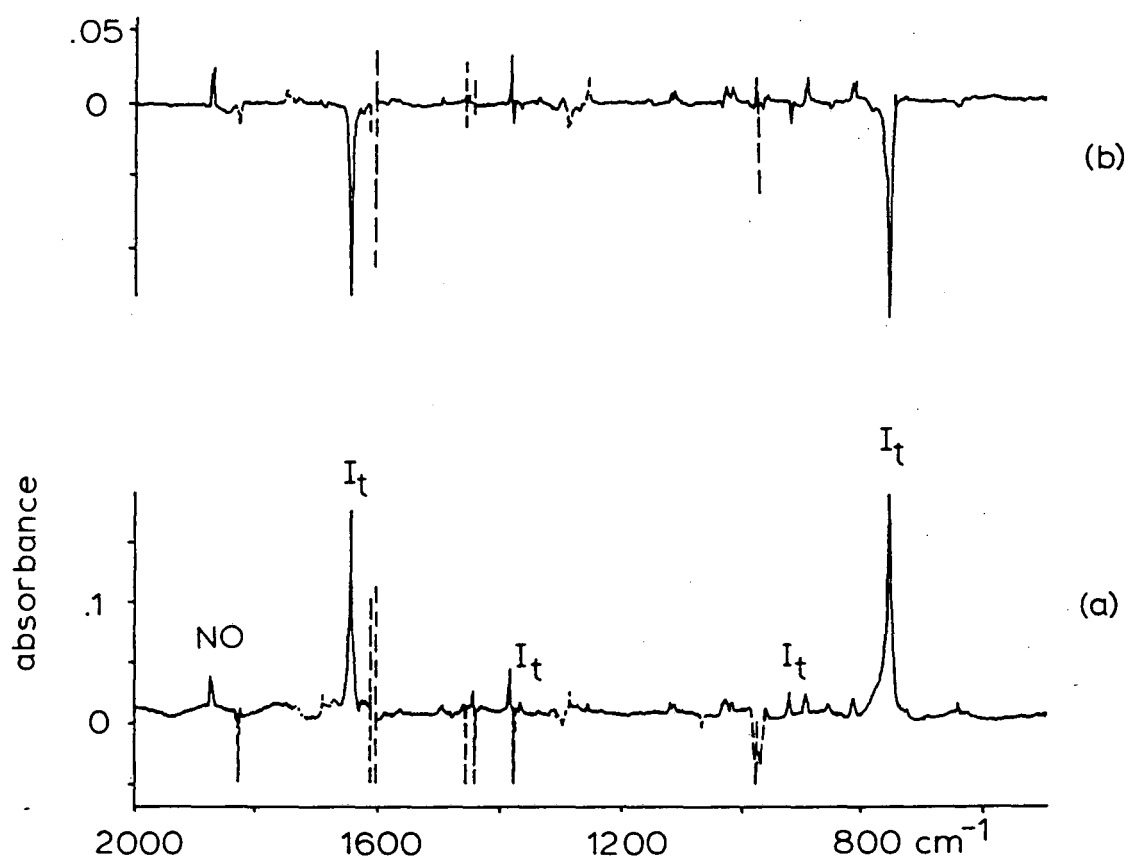
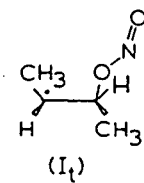
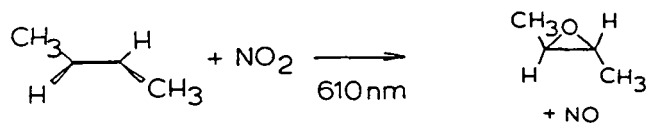
Scheme XI



Scheme XII



Scheme XIV



XBL 912-309

Fig. 1

$\text{C}_4\text{H}_8/\text{NO}_2/\text{Ar} =$
2.5/1/400

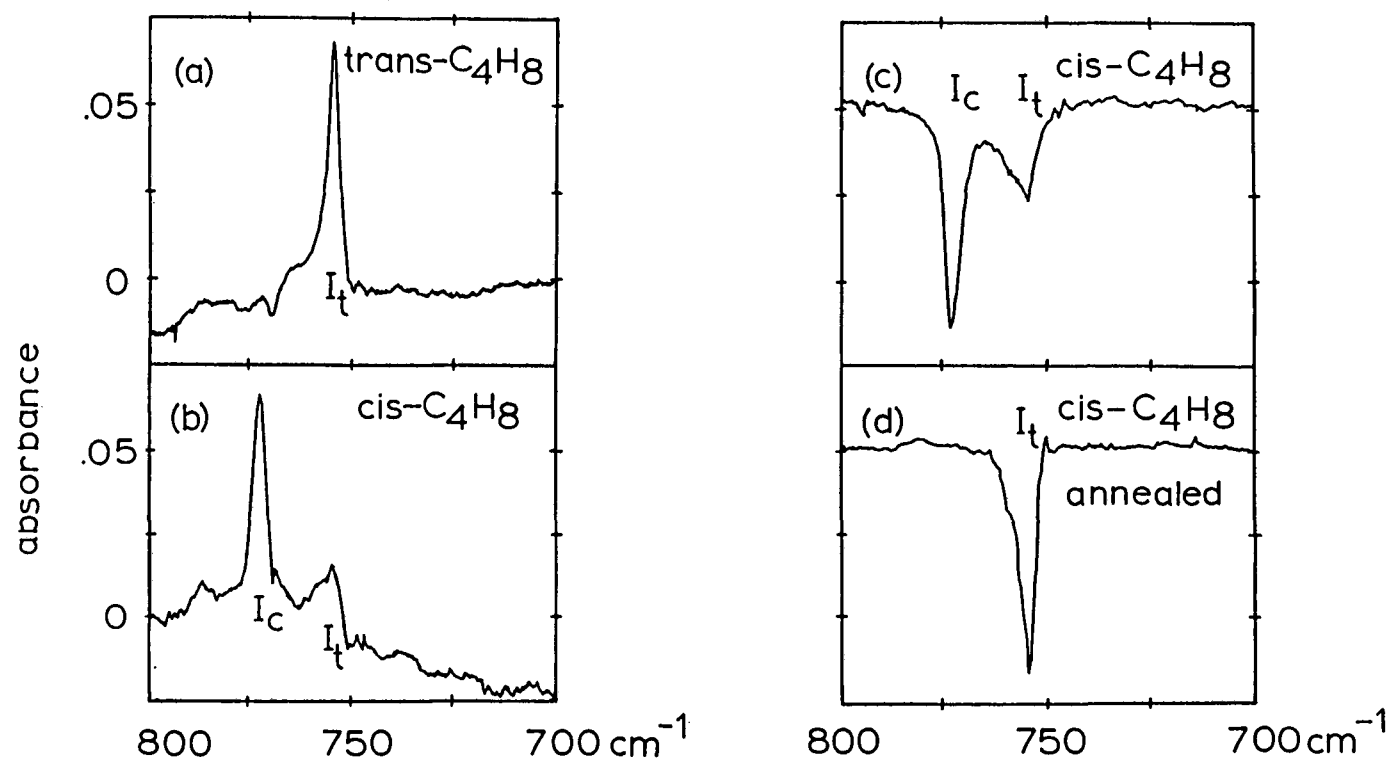
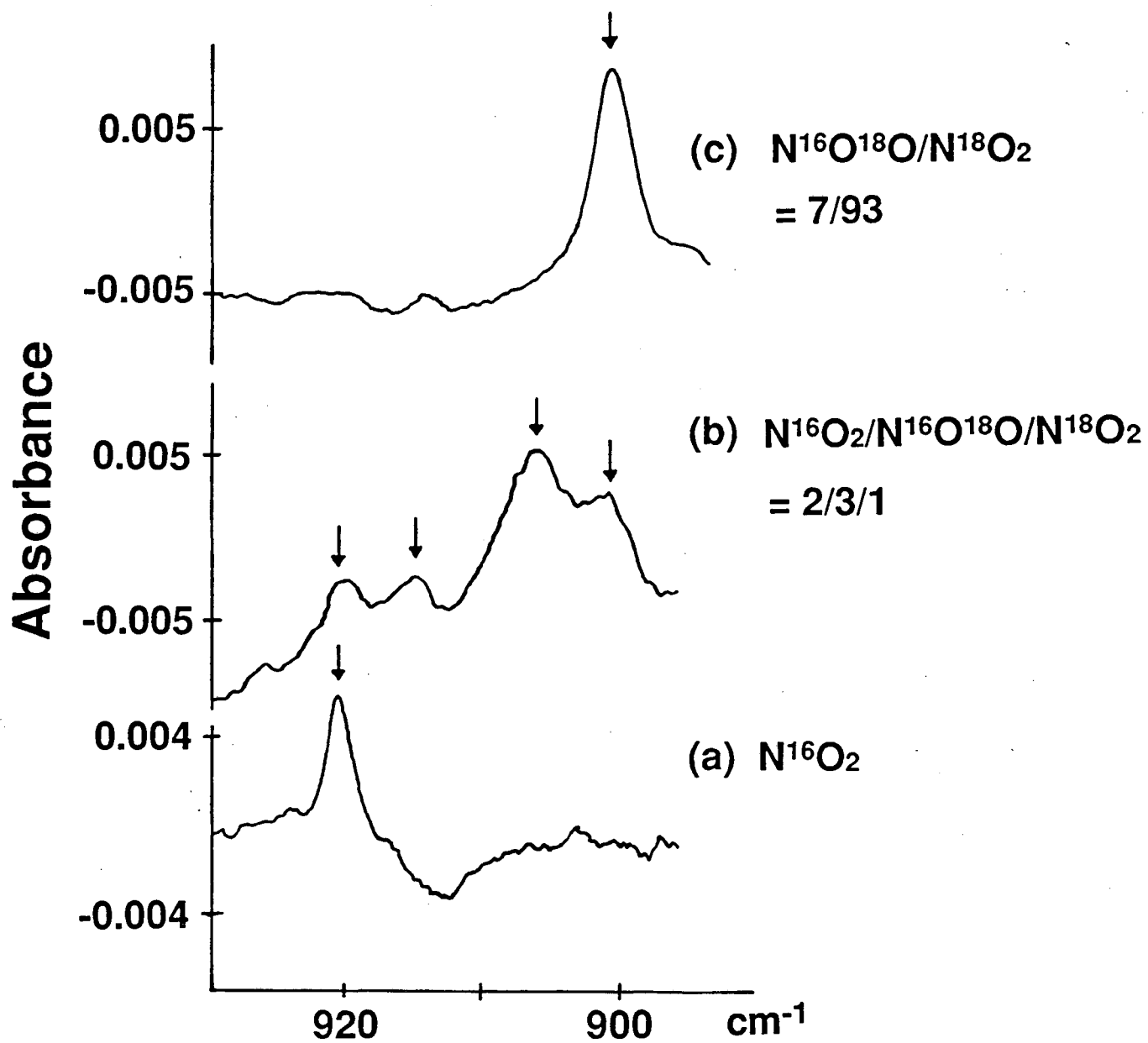


Fig. 2



XBL 887-2605

Fig. 3

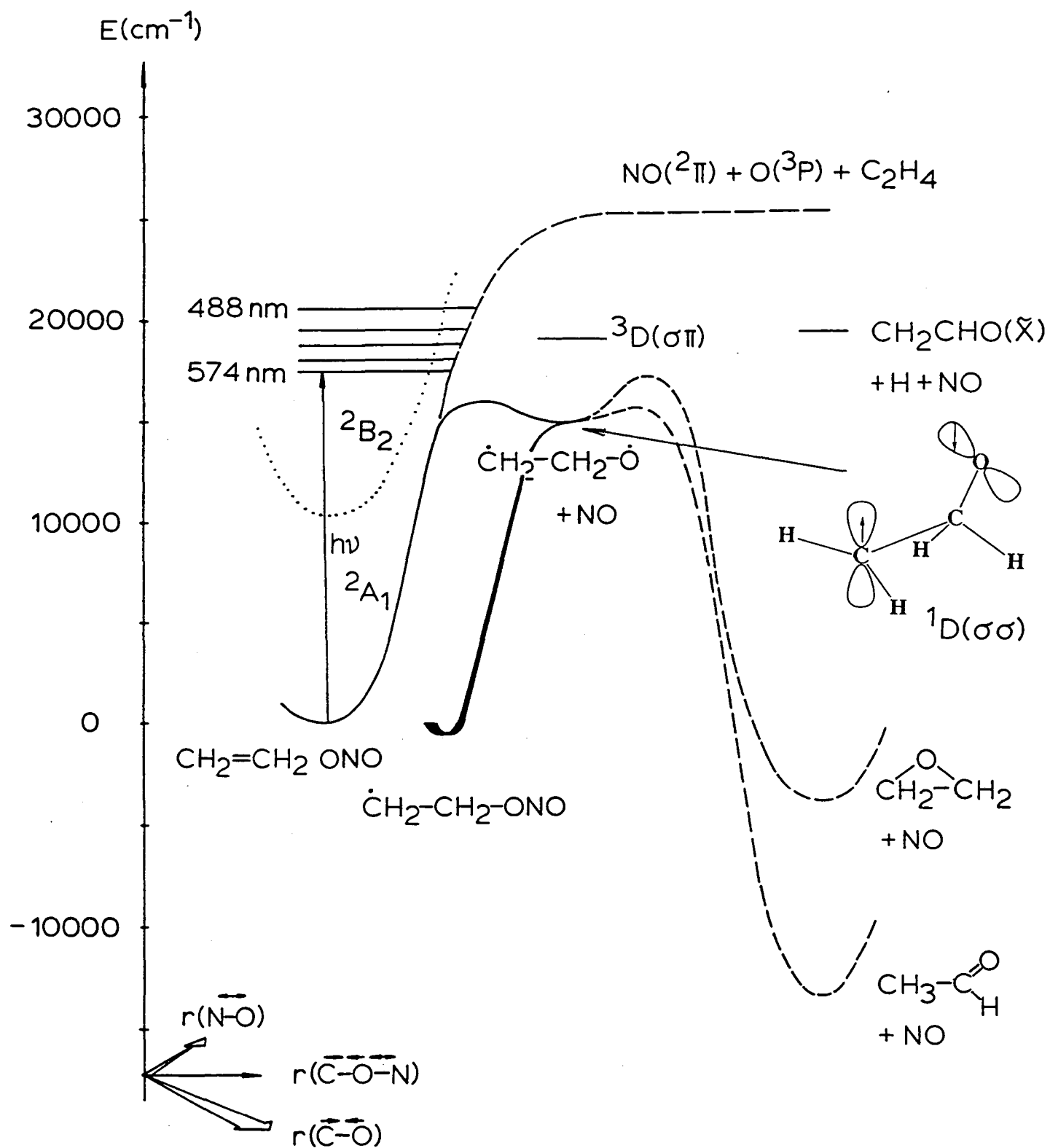
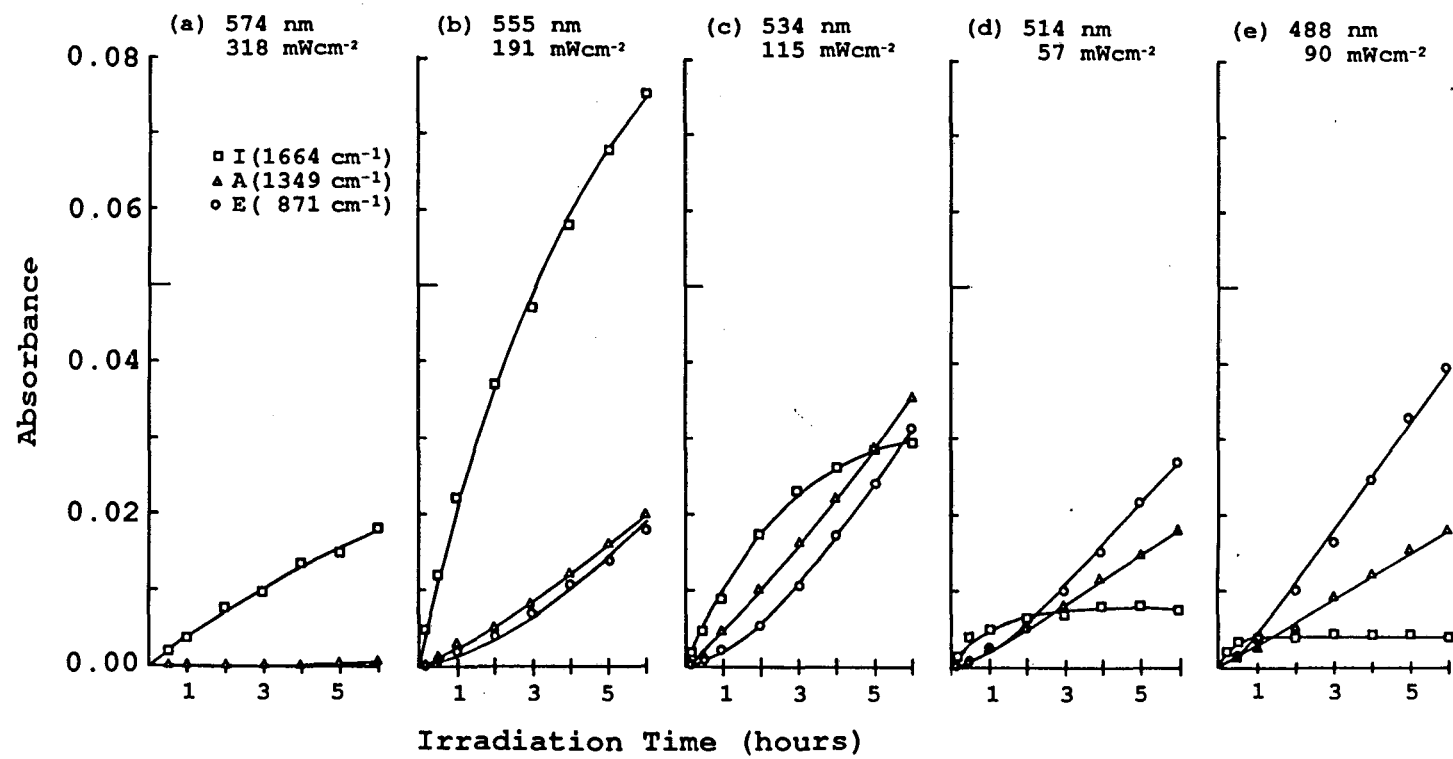


Fig. 4



XBL 8911-4285

Fig. 5

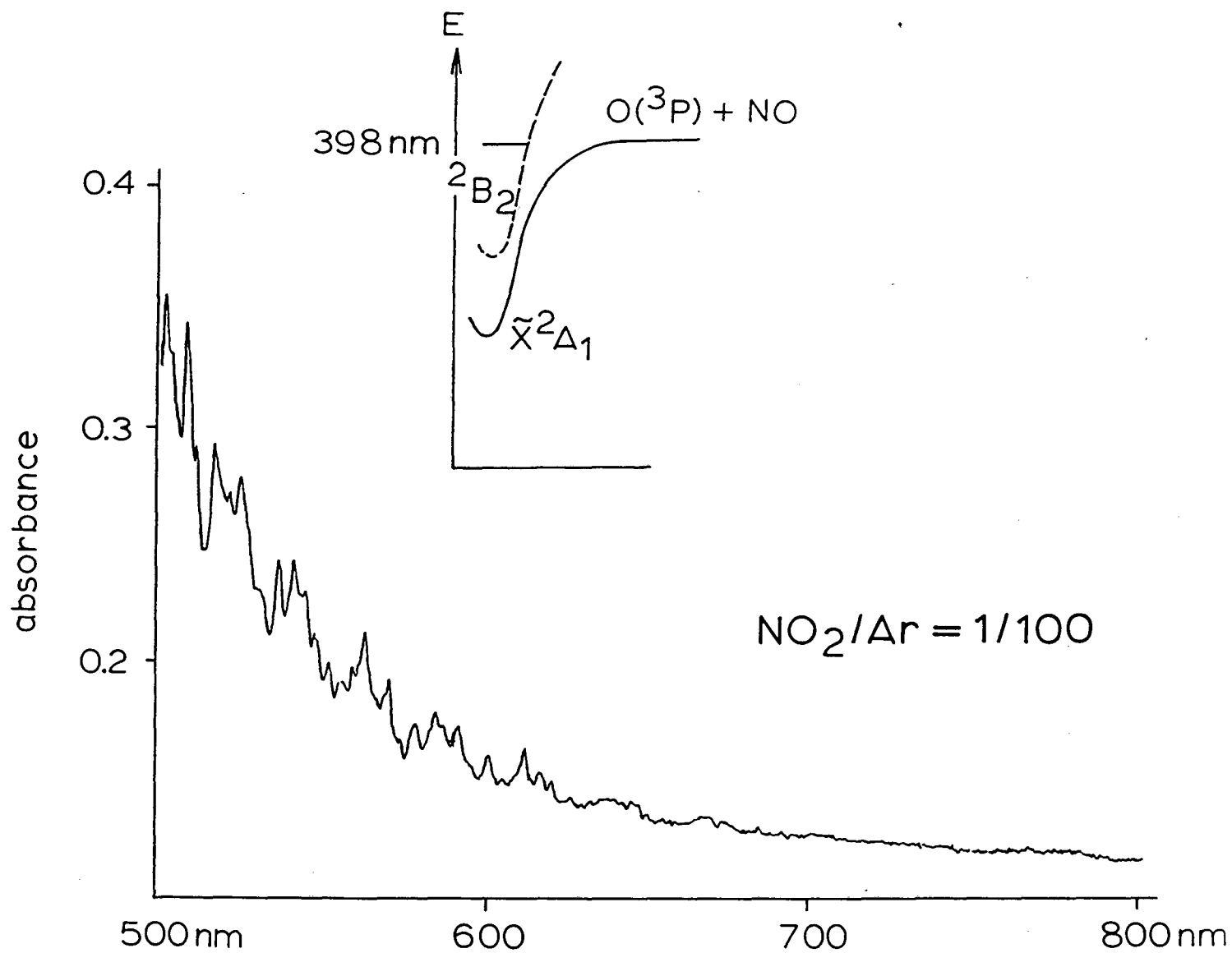
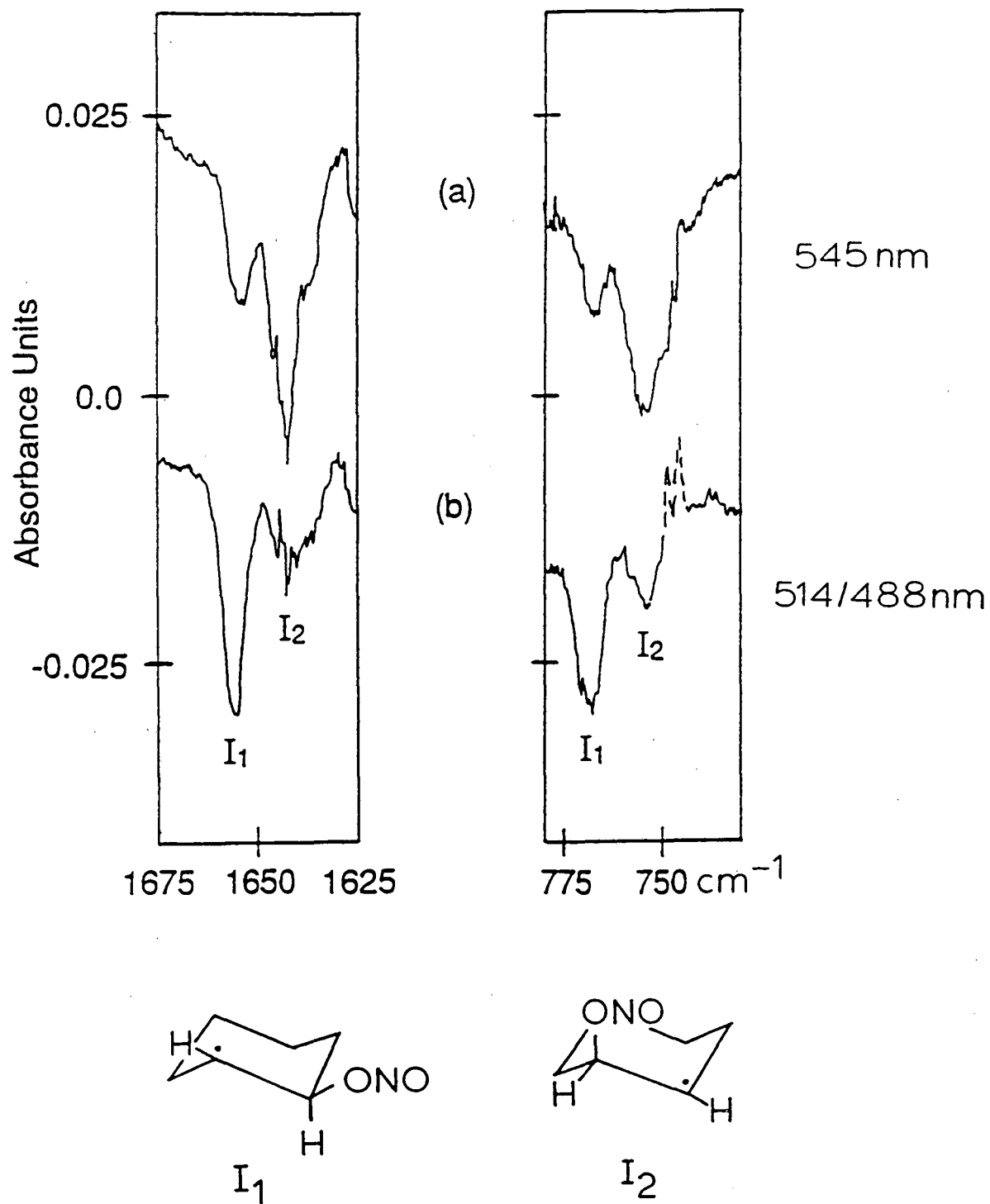
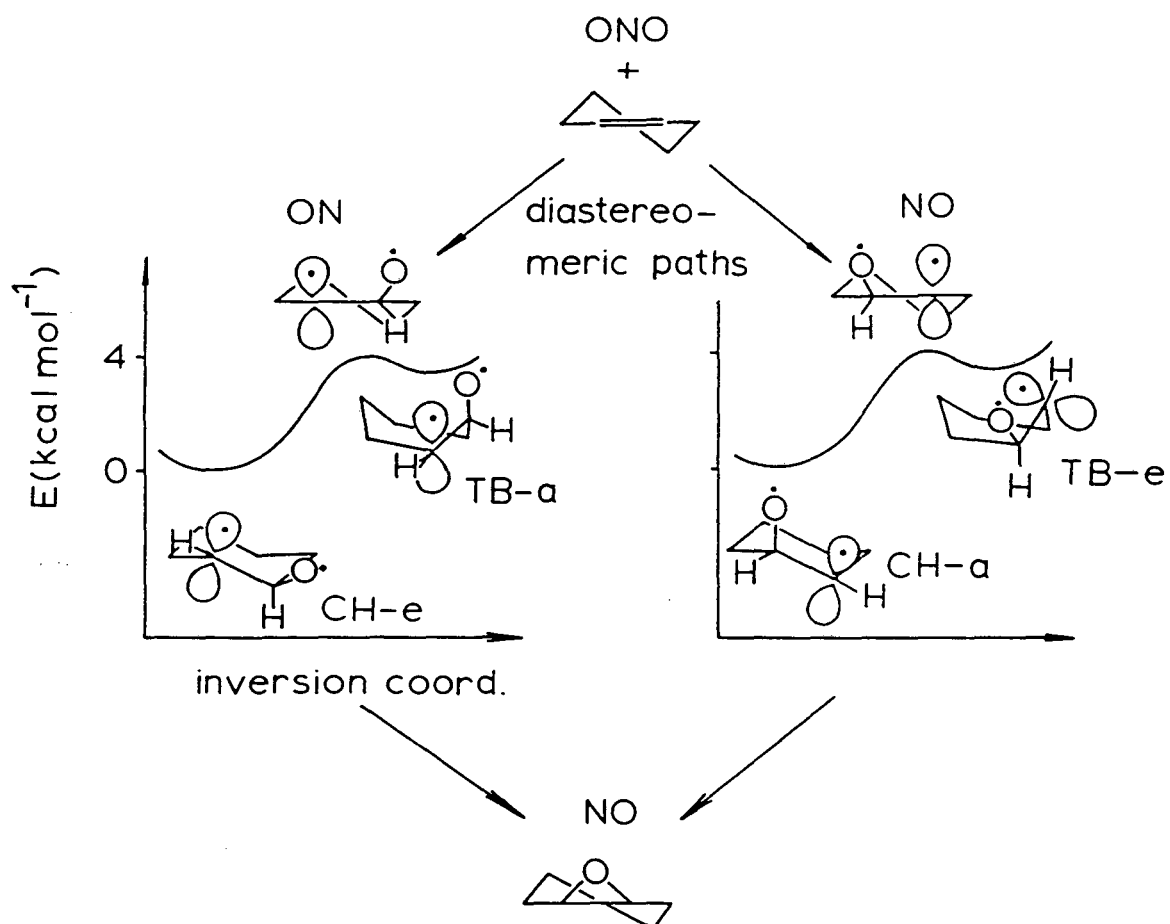


Fig. 6



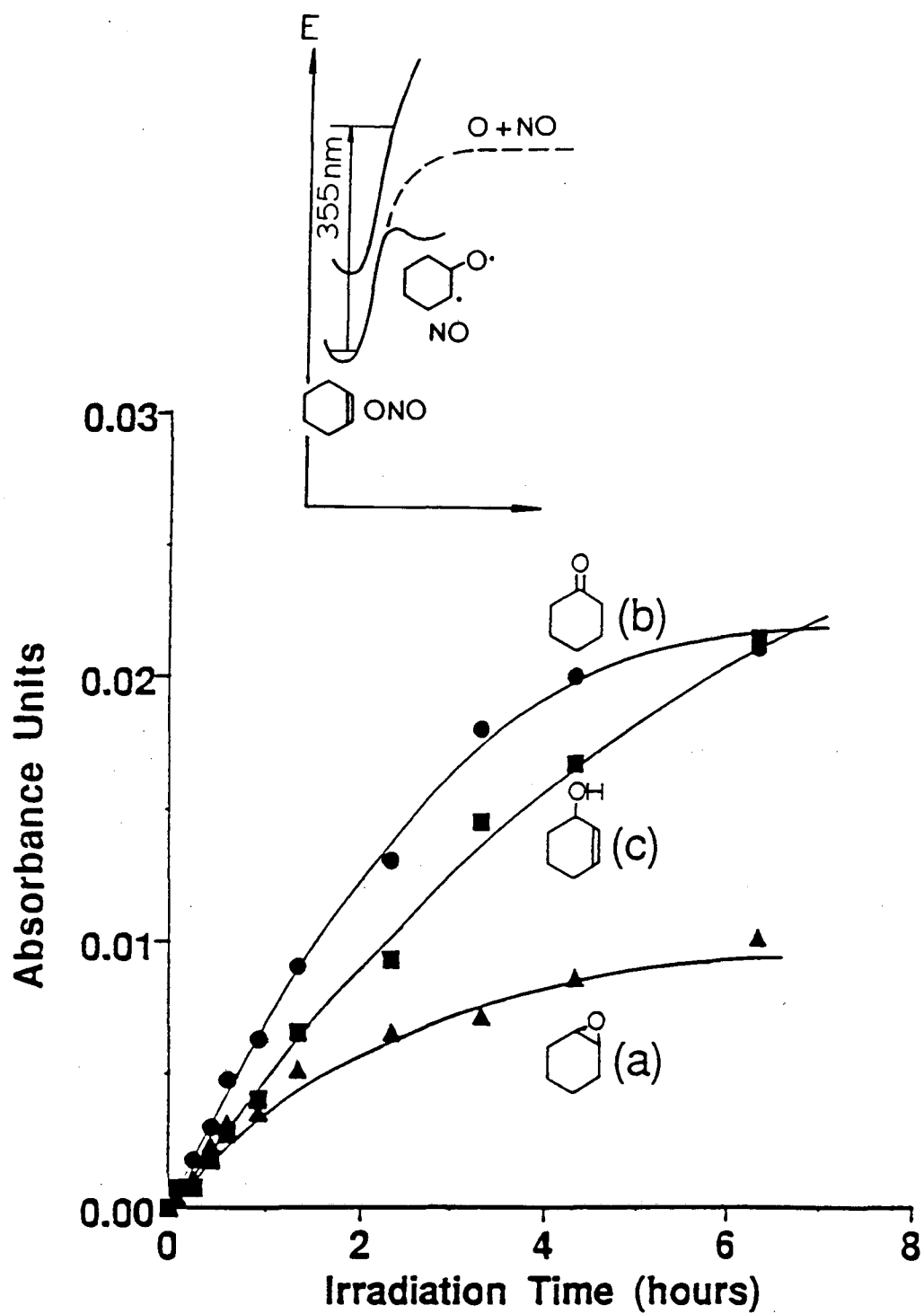
XBL 912-306

Fig. 7



XBL 912-305

Fig. 8



XBL 912-304

Fig. 9

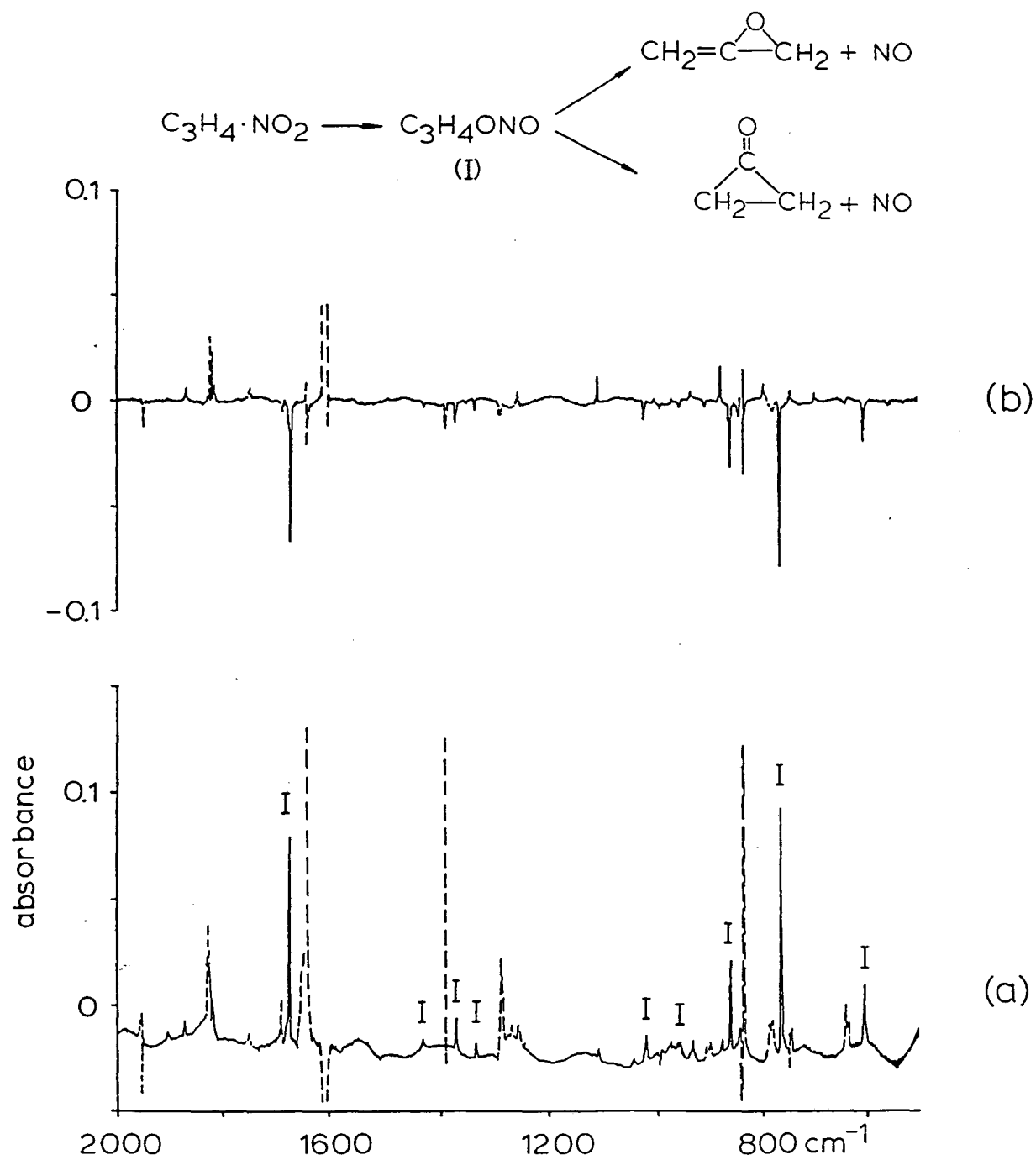


Fig. 10

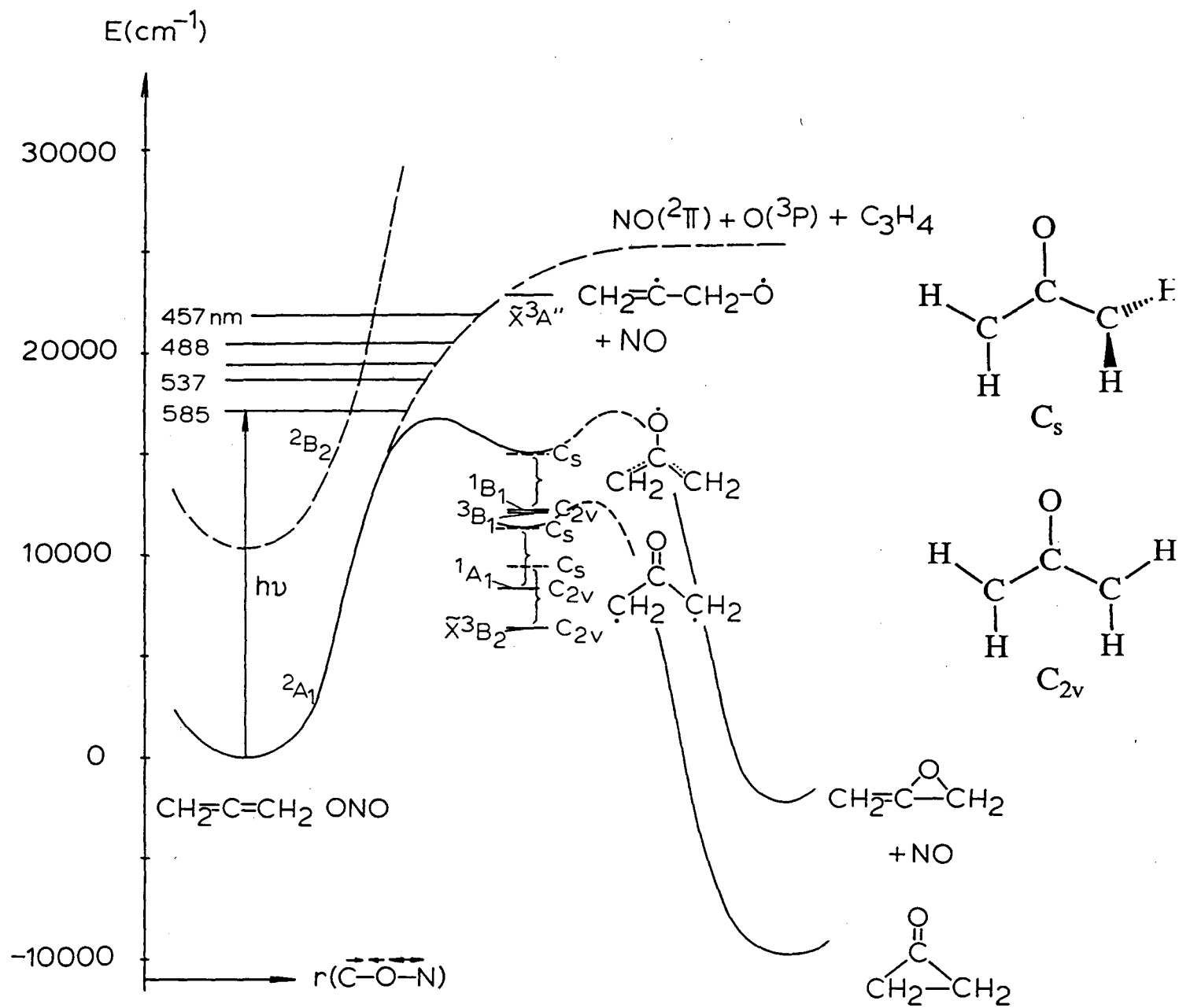


Fig. 11

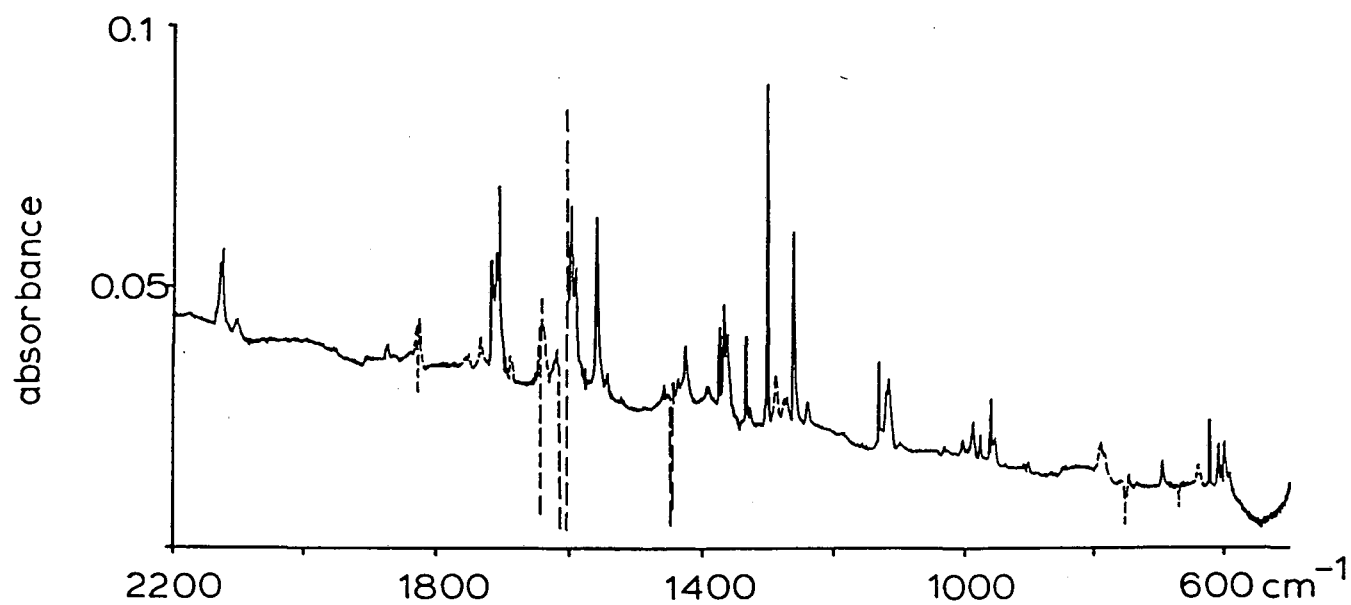
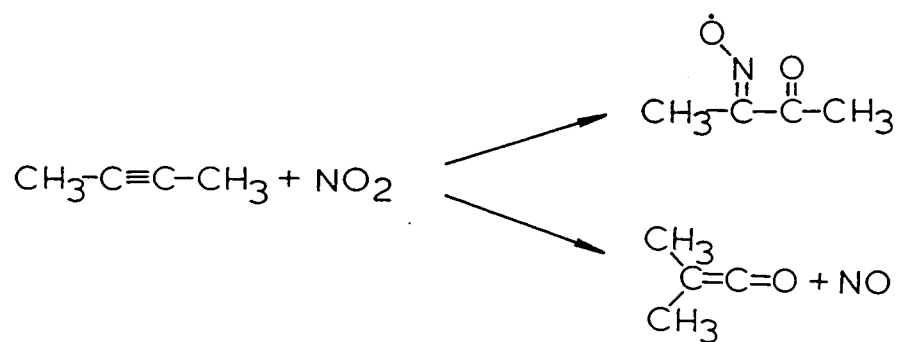


Fig. 12

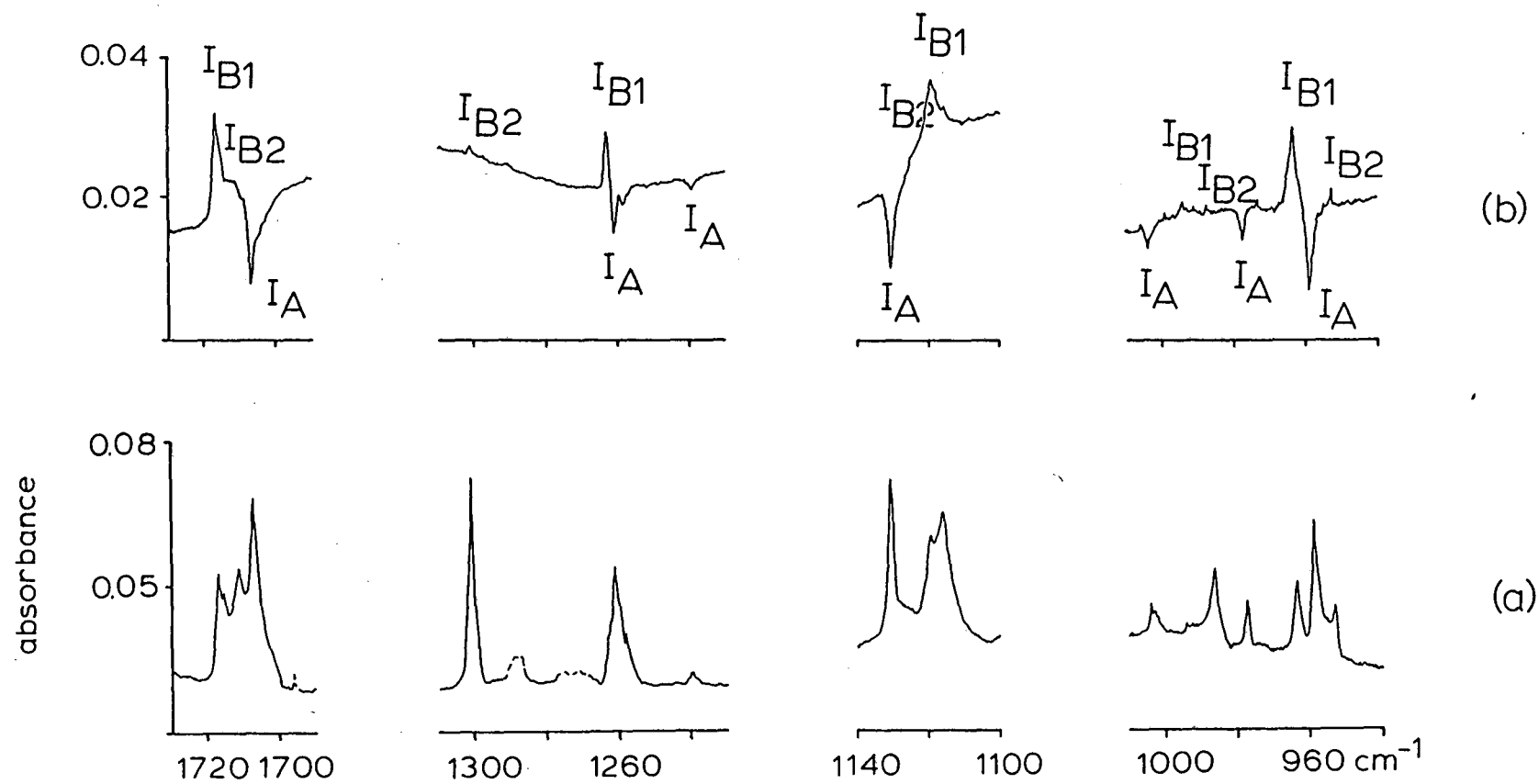
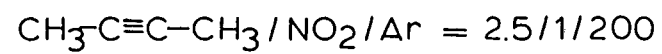


Fig. 13

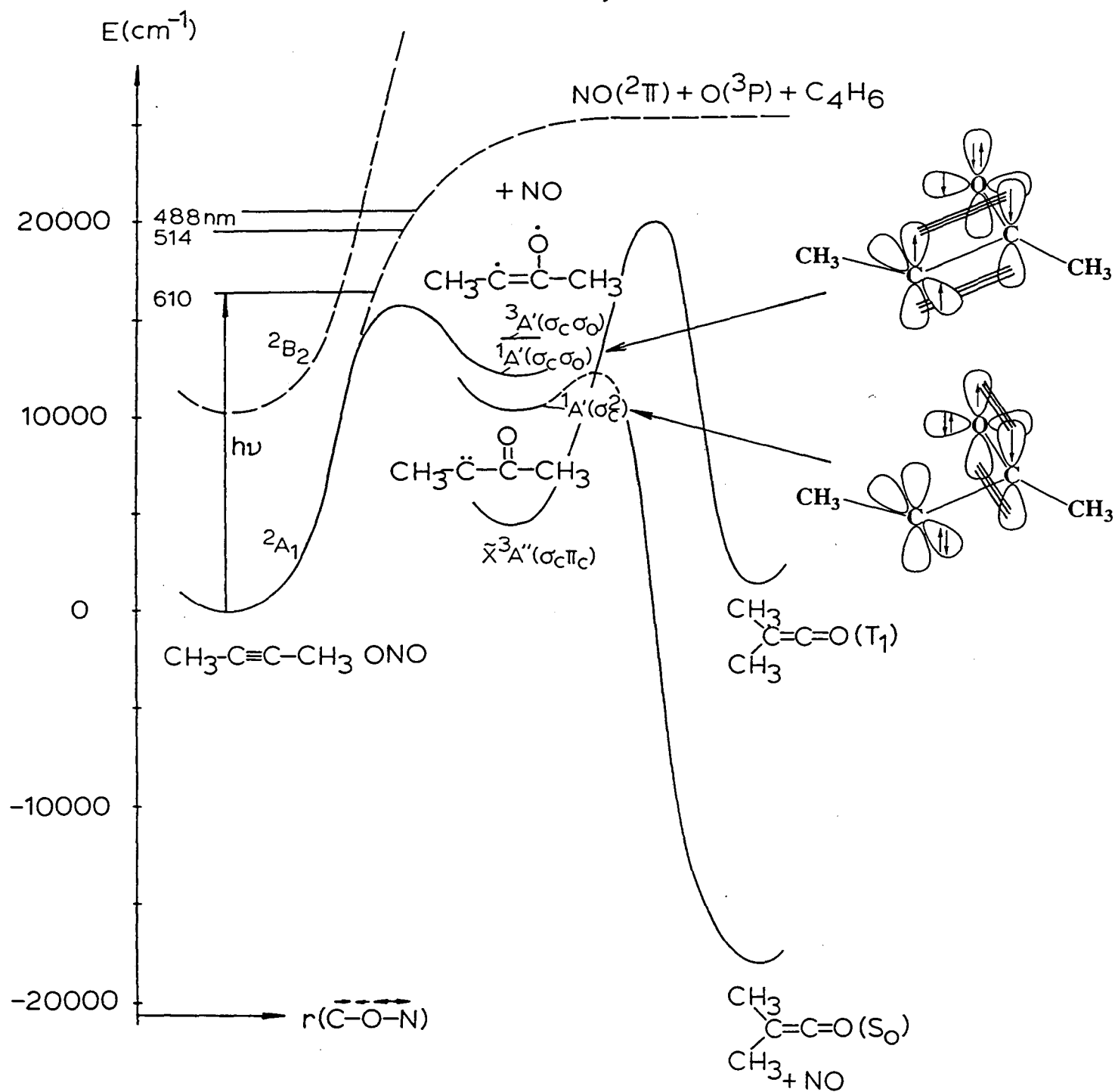


Fig. 14

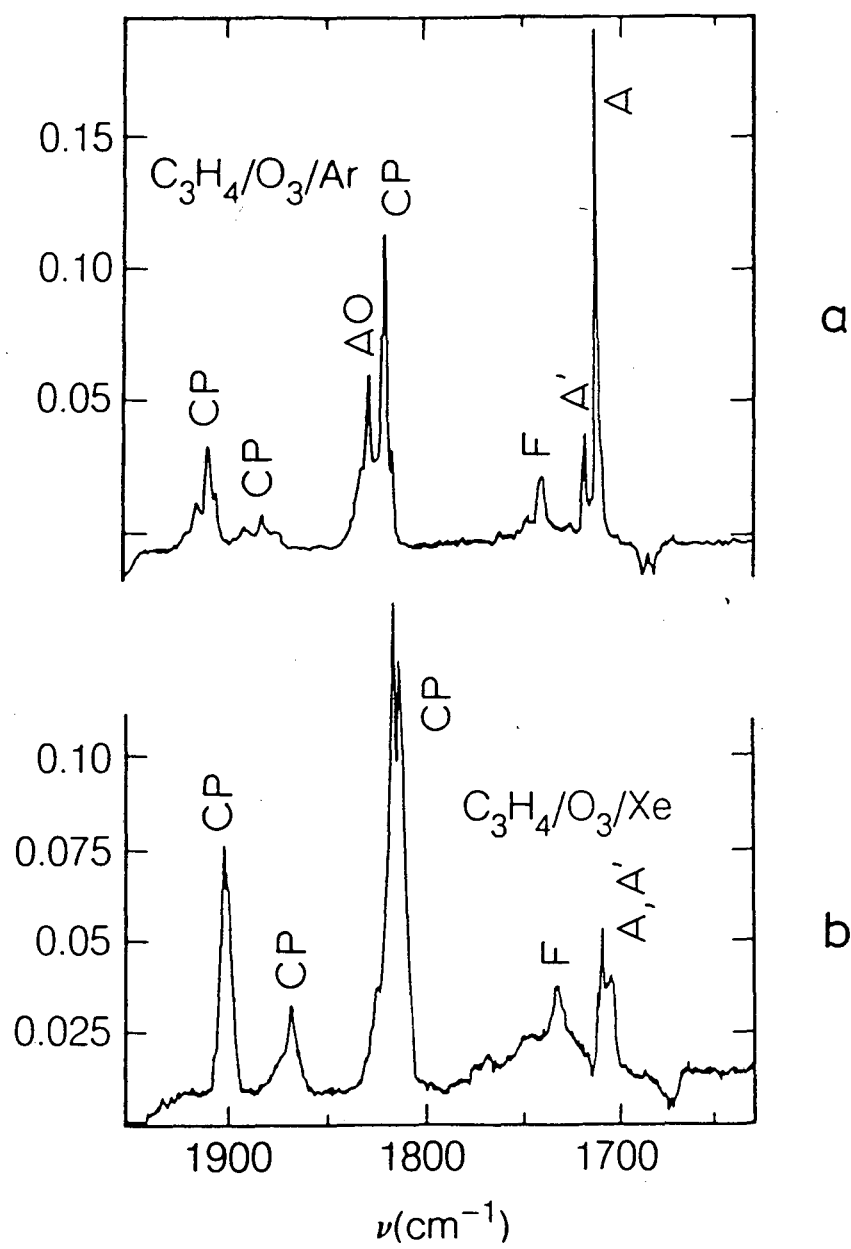


Fig. 15

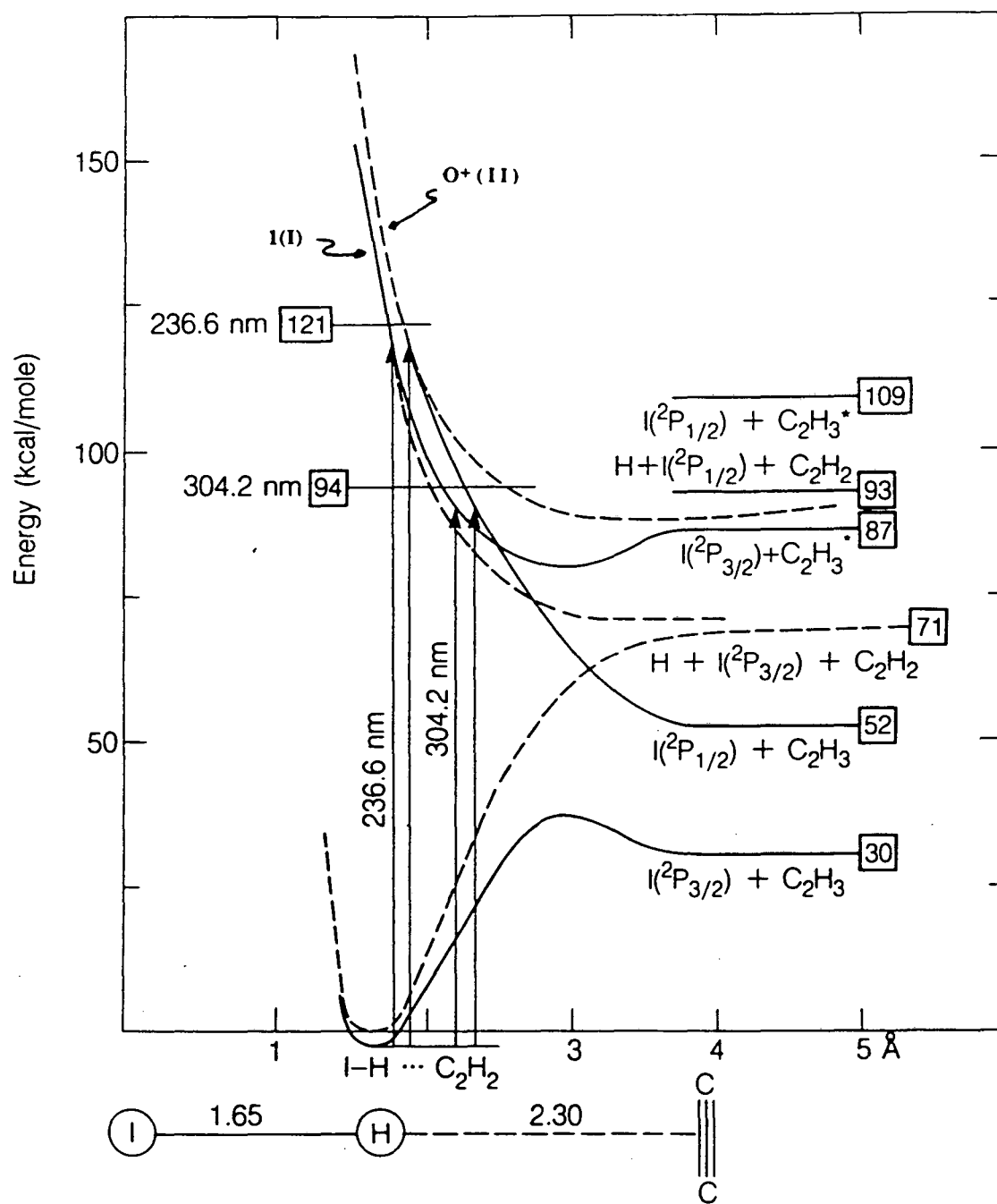


Fig. 16

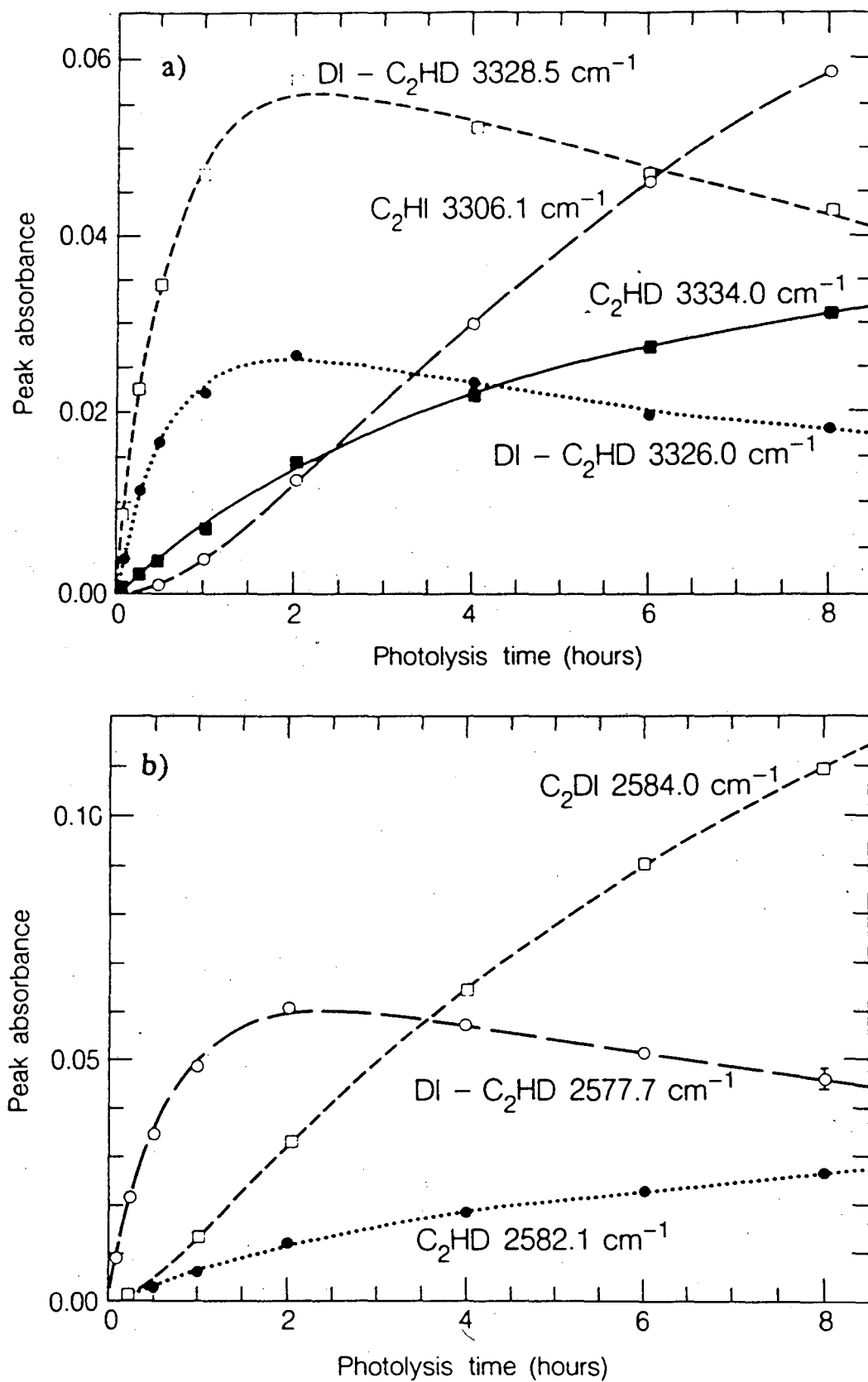


Fig. 17

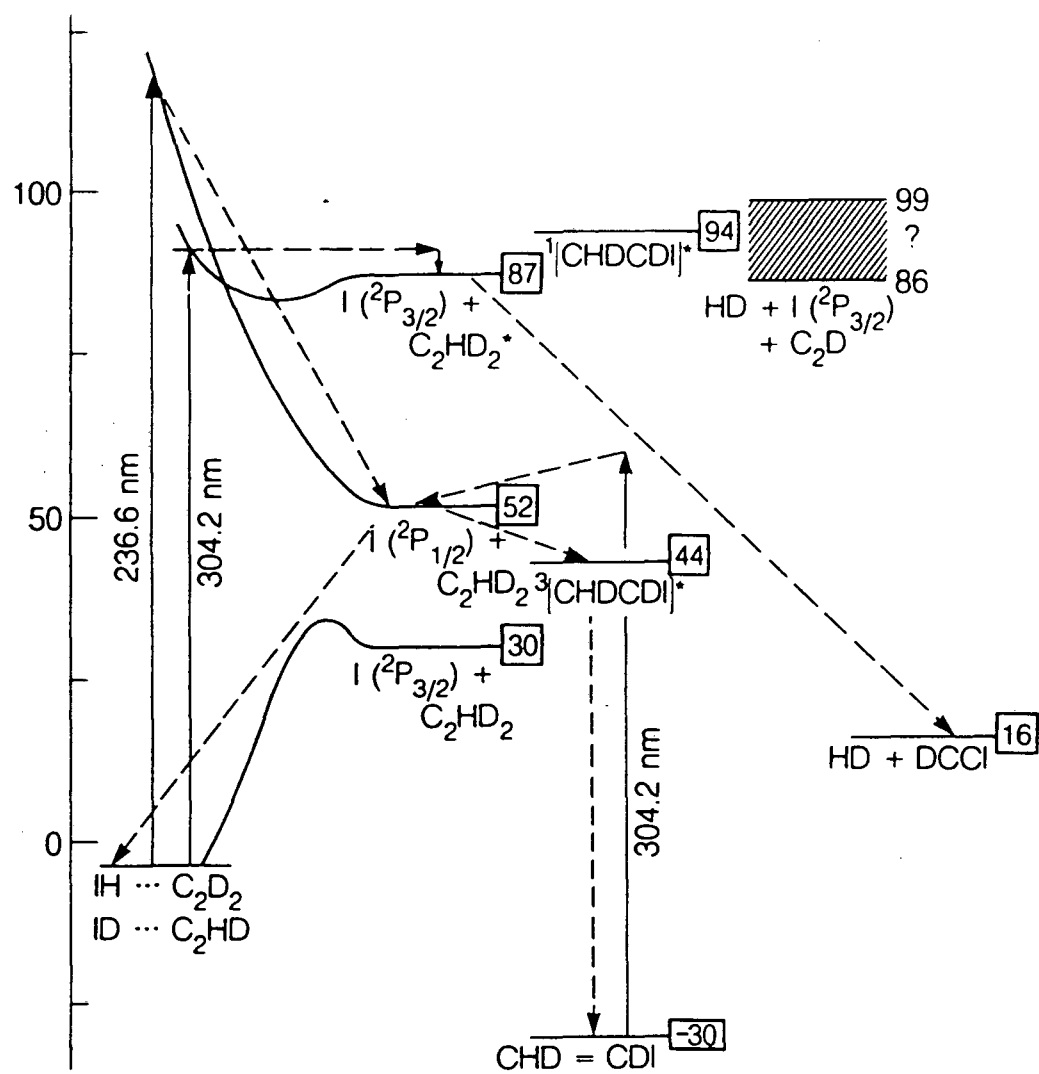


Fig. 18

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720