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Infrared Laser Techniques to Study the Structure and Dynamics of Transient Species

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Abstract

Infrared multiple photon laser induced chemistry has moved over the past ten years between the extremes of heralding truly intramolecular selective chemistry and being merely a laboratory curiosity. The maturing of infrared multiple photon excitation (IRMPE) now finds IRMPE used routinely in a variety of experiments including spectroscopy, chemical kinetics, thermodynamics and laser driven synthesis. Continuously tunable infrared laser sources now allow a much wider range of molecules to be excited, and the photophysics of IRMPE to be probed in greater detail, than was possible with only limited line tunability. Examples of both the photophysics of IRMPE and applications to kinetics and spectroscopy are discussed, including vibrational photodissociation spectra of isolated metal clusters.

Introduction

Infrared multiple photon chemistry has captured the imagination of chemists and physicists alike, for reasons ranging from the exotic possibilities of "mode-specific" chemistry to the intrigue of non-linear optics and explorations of "chaos." The original chaos in the field has to some extent waned due to a general consensus on the photophysics of IRMPE and failure to achieve the most ambitious goal of truly specific intramolecular chemistry. However, much of the work in IRMPE has been limited to narrowly tunable lasers at relatively few wavelengths, and non-specific probes of both the excitation process and reaction dynamics. Advances in laser physics are providing increased coverage of the infrared region with sufficient energy to drive multiphoton processes (e.g. optical parametric oscillators[1], Raman shifted dye lasers[2]), spectroscopic probes are providing detailed data on excited vibrational energy levels, and new in-situ probes allow dissociation kinetics to be followed directly. It is not too surprising that as more definitive experiments become available, commonly held descriptions of the intimate dynamics of IRMPE need to be modified. More important than simply redefining the physical description, recent experiments begin to realize the potential ir laser chemistry has always promised. IRMPE can conveniently be used to produce free radicals for characterization, and their subsequent chemistry studied over a range of temperatures. IR photodissociation spectroscopy is providing the first vibrational spectra of naked metal cluster molecules, whose transient existence makes them difficult to study by conventional techniques. In a synergistic fashion, metal cluster chemistry may allow new molecules to be synthesized for strict tests of IRMPE theories. In this paper we will address several topics. Comparison of multiple photon overtone spectroscopy with overtone spectra is used to elucidate details of IRMPE. The use of infrared laser driven chemistry for free radical characterization and kinetics will be illustrated, and application of IRMPE to obtain vibrational spectra of metal clusters will be discussed.

Excited State Resonances in IRMPE

Infrared multiple photon dissociation spectra have typically been singularly uninformative, usually due to the coarse resolution afforded by CO_2 lasers and their limited frequency coverage. On the one hand it is puzzling that frequency dependences of excited vibrational states did not appear, yet perhaps not surprising given the available resolution and density of potentially accessible molecular states. The picture of IRMPE most often used is illustrated in Fig. 1a[3]. Excitation is initially coupled into a molecule through some absorption feature, and once the molecule is energized the high density of vibrational states guarantees resonance for all successive absorptions. Yet for some molecules, at intermediate energies the vibrational state density is limited and specific excited state resonances occur. This is illustrated in Fig. 1b.

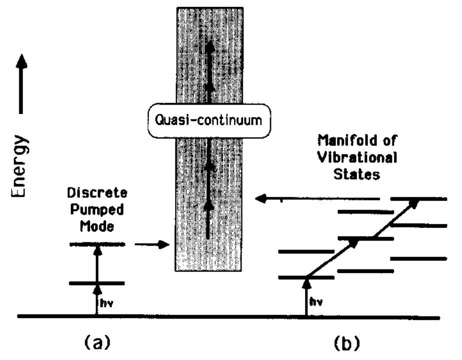
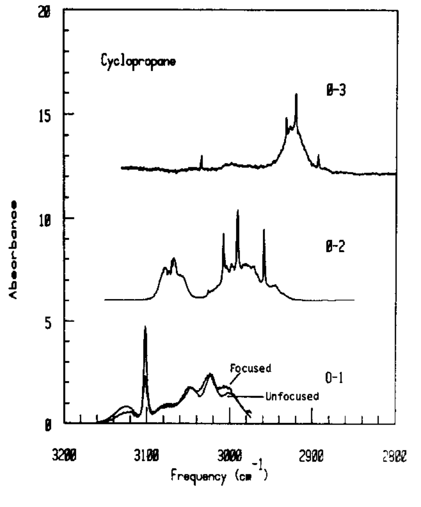


Fig. 1 Schematic diagram of infrared multiple photon excitation. (a) Excitation into pump mode followed by excitation through the quasicontinuum of vibrational states. (b) Excitation in which resonances with specific excited vibrational states strongly participate in an harmonic excitation ladder.

With the advent of continuously tunable infrared lasers, resonance effects are indeed observed. The effects of resonance were observed in 3μm excitation of ethyl chloride[4], and subsequently in 3μm excitation of propylene[5]. Resonance effects with 10 μm excitation are observed using high pressure continuously tunable CO_2 lasers[6].

The observed resonances can be understood by considering the manifold of excited vibrational levels available in an energized molecule, as elucidated by overtone spectroscopy. Fig. 2 illustrates the 3μm optoacoustic spectrum of cyclopropane under both low and high fluence.



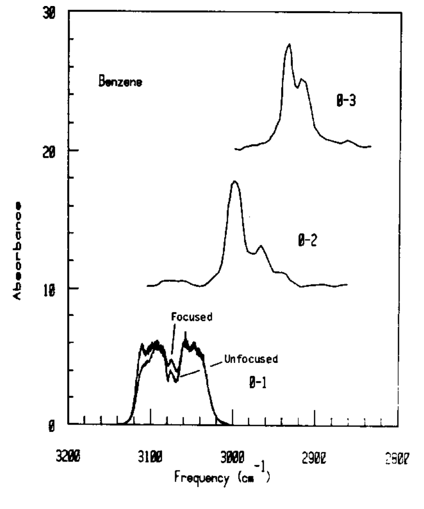


Fig. 2 Focused and unfocused optoacoustic spectra of cyclopropane in the 2800-3200 cm^{-1} region. Focused radiation produces a fluence of ca. 2 Jcm^{-1}. Overtone spectra (frequency axis normalized for the number of photons required to reach the overtone state) are included for comparison.

Fig. 3 Focused and unfocused optoacoustic spectra of benzene in the 2800-3200 Overtone spectra, normalized as in Fig. 2, are included for comparison.

An optical parametric oscillator is used in these experiments[5]. Enhancements in the high fluence spectrum are seen in the 3000-3050 cm^{-1} region, while the sharp Q-branch at 3100 cm^{-1} is reduced in amplitude. The latter feature is understood in terms of saturation of the multiphoton process while the enhancement at lower frequency indicates enhanced absorption. Comparison of the multiphoton spectrum with overtone spectra for the C-H stretch (Fig. 2) region[7] reveals the origin of the enhancement. To compare directly the infrared and higher frequency spectra, the frequency scale of the overtone spectra are divided by the number of infrared photons required to reach that frequency; that is the first overtone is divided by 2 and the second by 3. From Fig. 2 it is apparent that a harmonic ladder at 3010 cm^{-1} is available to up to v=3, built on the ν , C-H stretch. In contrast, the 3100 cm^{-1} ν_5 stretch has no accessible ladder (matching overtone states) and as a result tends to saturate relative to the 3010 cm^{-1} absorption. In general, the lack of an accessible facile excitation ladder for the highest frquency fundamental vibration is due to the absence of any v=2 state with energy equal to twice that frequency. All v=2 states are lower in energy because of either anharmonicity or lower fundamental frequencies.

The general nature of resonances in IRMPE is further demonstrated in data for benzene. Optoacoustic spectra under low and high fluence conditions are shown for benzene in Fig. 3, along with the corresponding overtone spectra[8]. An enhancement is observed at 3075 cm^{-1}, corresponding to overlap with the first overtone band. Similarly "doorway states" have been found in 10μm excitation, including states identified as two-photon transitions, combination bands and overtone states[6]. Knowing which states can optimally contribute to a multiple photon ladder, coupled with their identification via the spectroscopy of excited vibrational states allows some ability to predict infrared multiple photon excitation and design molecular structures (chromophores) for optimal IRMPE.

Reaction Dynamics

In addition to the complex problem of understanding the photophysics of IRMPE, studies of infrared multiple photon induced reactions are typically subject to the same problems which have historically plagued all studies of thermally induced reactions, one of which is detection of transient free radical species which are the reaction products of homolytic bond cleavage. Similarly, the lack of direct in-situ probes of reaction products has prevented more general utilization of infrared laser chemistry to induce homogeneous, short residence time, high temperature chemistry. Multiphoton ionization (MPI) is a relatively new technique which allows species selective, in-situ detection of free radicals with good time resolution. In MPI, an intense visible or ultraviolet laser is used to ionize a molecule, typically via a 2-5 photon process[9]. Species specificity is obtained through resonances with intermediate electronic states, and the use of pulsed laser sources provides good time resolution. The ability of MPI to detect fairly complex radicals and radicals which do not fluoresce provides significant advantages over laser induced fluorescence. MPI coupled with mass analysis can provide enhanced species selectivity and background suppression, with superior time resolution compared to conventional mass spectroscopy.

MPI has been used to elucidate reactions occuring in CH_3OH thermal chemistry. The most likely thermal reactions of CH_3OH are listed below:

	Δ H(kcal/mole)
$CH_3OH \rightarrow H_2CO + H_2$	33.6
$CH_3OH \rightarrow CH_3O + H$	104.4
$CH_3OH \rightarrow CH_3 + OH$	92.3
$CH_3OH \rightarrow CH_2OH + H$	94.2
$CH_3OH \rightarrow HCOH + H_2$	71
$CH_3OH \rightarrow CH_2 + H_2O$	92

CH_2OH can be formed from CH_3OH by direct C-H bond cleavage or by subsequent hydrogen abstraction reactions. The top panel of Fig. 4 shows the MPI spectrum of CD_2OH formed by infrared muliple photon dissociation (IRMPD) of CD_3OH[10].

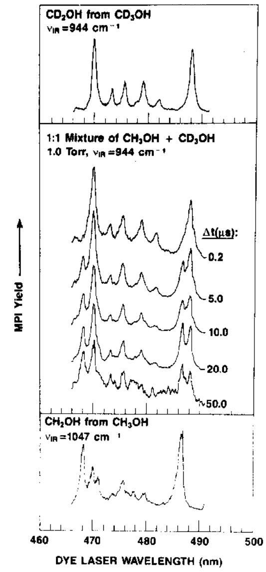


Fig. 4. Top panel: MPI spectrum of CD_2OH after IMPD of CD_3OH at 944 cm^{-1}[12]. Center panel: MPI spectra of CD_2OH and CH_2OH as a fuction of time following IRMPD of a 50/50 mixture of CD_3OH and CH_3OH at 944 cm^{-1}. Bottom panel: MPI spectrum of CH_2OH after IRMPD of CH_3OH at 1047 cm^{-1}.

This spectrum is taken promptly after an infrared laser pulse at 944 cm^{-1}. Dissociation of CD_3OH in a 50/50 mixture of CD_3OH and CH_3OH (middle panel, Fig. 4) as a function of the time between the infrared laser pulse and detection pulse shows the growth of a second spectrum identified as CH_2OH, as hydrogen abstraction occurs from CH_3OH. A spectrum of CH_2OH formed from dissociation of CH_3OH at 1047 cm^{-1} is shown in the bottom panel of Fig 4. From the measured time evolution of the spectra in Fig. 4 a rate constant of 10^{-12} cm^{3}mol^{-1}sec^{-1}is obtained for hydrogen abstraction from CH_3OH, in reasonable agreement with literature values for hydrogen abstraction by OH.

In addition to direct observation of CH_2OH kinetics, information on the vibrational frequencies of CH_2OH are also determined in the experiment. Excess vibrational energy in the reaction products produces hot bands in the MPI spectrum.

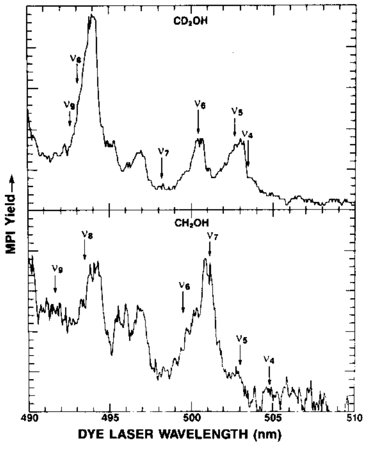


Fig. 5. Detailed view of the MPI spectra of CH_2OH and CD_2OH in the hot-band region, 490-510 nm. Arrows indicate positions of predicted hot-band transitions[11].

These are shown in Fig. 5 for CH_2OH and CD_2OH produced by IRMPD of CH_3OH and CD_3OH, respectively. Also shown in Fig. 5 are the locations and assignments of vibrational frequencies determined from matrix isolation studies[11]. Agreement is quite good, with deviations occuring predominantly for the ν_8 vibrational mode which may have been perturbed in the matrix. It is interesting to note that from the hot band spectra, the maximum internal energy content is implied to be about 1300 cm^{-1}, or about 1.3 ir photons. Little excess energy in CH_2OH suggests that extensive secondary photolysis does not take place, dissociation takes place relatively close to threshold, and that the bulk of the hydrogen abstraction exothermicity is disposed of either in product translational energy or vibrational energy of the other product.

While MPI detection of IRMPD reaction products can be quite powerful, relatively few radicals have been characterized by this technique. Some of the larger polyatomic radicals characterized to date include NH_2, CH_3, CF_3, CH_2F, CH_2OH, allyl, benzyl, cyclohexyl, cis and trans-1-methyl allyl, 2-methyl allyl and CH_3OCH_2[12]. As MPI is demonstrated for additional radicals, MPI will become a broadly applicable technique for probing reaction dynamics. Conversely, IRMPD may play a role in providing selected radicals for characterization. Table 1 lists radical intermediates which are inferred in IRMPD of selected hydrocarbons based on ex-situ stable product analysis[13].

Table 1. Radicals formed by 3 μm IRMPD of selected hydrocarbons.

Radical	Precursor
CH_3	C_2H_6
C_2H_5	C_2H_6, C_3H_8, C_4H_{10}
$CH{=}CH_2$	C_3H_6
$CH_2{=}CHCH_2$	C_3H_6, 1-C_4H_8
$CH_3CH{=}CH$	2-C_4H_8

Direct IRMPD is uniquely suited for radical preparation, since the radical can be produced in a relatively isolated environment. Observation of products consistent with addition and recombination reactions of the radicals in Table 1 implies that the radicals are produced without excessive vibrational excitation. The radicals (and their kinetics) can subsequently be probed with time resolved diagnostics.

IR Photodissociation Spectroscopy of Metal Clusters

If infrared laser induced chemistry has failed to realize the original expectations of revolutionizing selective chemistry, it has succeeded in providing new tools to study transient molecules in low concentrations generally not amenable to infrared spectroscopy. Photodissociation spectra of ions[14] and van der Waals complexes[15] provide information on their vibrational spectra which cannot be obtained by conventional absorption techniques. For large molecules, the ability to excite molecules slowly compared to unimolecular reaction rates allows identification of lowest energy reaction pathways[16]. This is particularly important for species such as ions whose thermal chemistry is difficult to obtain.

Metal clusters are a new class of transient molecules whose structure and reactivity are only beginning to be explored. As metal clusters are reacted with an increasingly broad range of reagents, the question of the structure of the metal cluster-adsorbate complex becomes critical to understanding the chemistry and comparing cluster induced chemistry to analogous "traditional" chemistries (e.g. surface chemistry, organometallic reactions, isolated molecule reactions).

IR photodissociation has now been applied to metal clusters to obtain vibrational spectra for iron clusters reacting with methanol[17]. Iron clusters are formed by well established laser vaporization/molecular beam techniques. The clusters enter a reaction zone containing methanol forming cluster-methanol adducts. Clusters and adducts are detected by photoionization time-of-flight mass spectroscopy. Fig. 6 shows the photodissociation spectrum of $Fe_8(CH_3OH)$ obtained using a CO_2 TEA laser as the photodissociation source.

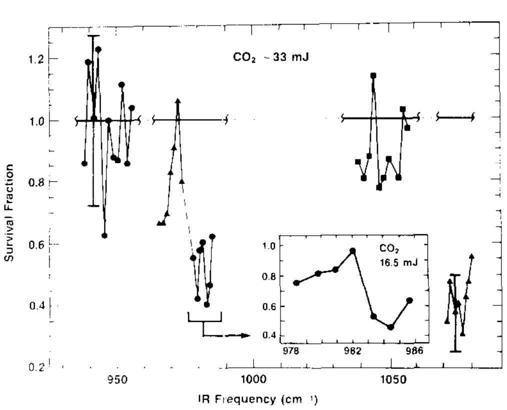


Fig. 6. IRMPD spectrum of $Fe_8(CH_3OH)$. The insert displays the results for reduced power dissociation in the 978-986 cm^{-1} region.

The survival fraction is the ratio of the ion signal for a cluster with radiation to the signal for that cluster without radiation. Only clusters containing methanol are depleted; bare metal clusters are unaffected by the infrared radiation. Similar spectra are obtained for all clusters containing up to 12 iron atoms. The 985 cm^{-1} feature is assigned to the

CO stretch of chemisorbed CH_3O, in agreement with results from bulk surface studies[18]. The 1075 cm^{-1} feature is consisent with an Fe-H stretch for bridge-bonded hydrogen on an iron surface[19]. These results therefore imply that CH_3OH dissociatively adsorbs on iron clusters to form chemisorbed CH_3O and hydrogen atoms.

The IRMPD of metal clusters provides a unique capability to probe infrared multiple photon photophysics because of the ability to alter molecular structure by simply varying cluster size and the number of adsorbates. Effects of varying the density of states by increasing cluster size will be readily probed in a more systematic fashion than is usually possible. Fig. 7 shows initial data on the fluence dependence of iron-methanol clusters for clusters with varying numbers of iron atoms and one or two adsorbed methanol molecules.

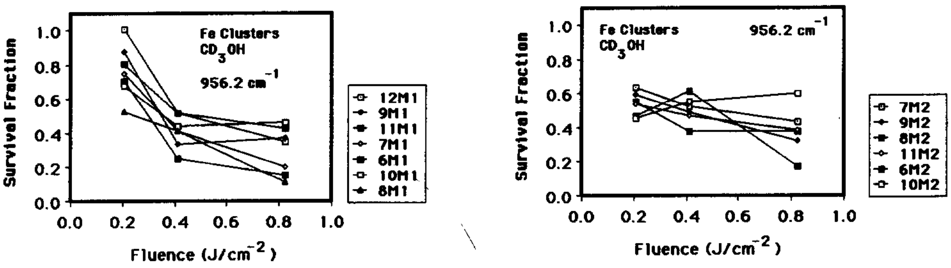


Fig. 7. Fluence dependence of IRMPD of $Fe_x(CD_3OH)$ and $Fe_x(CD_3OH)_2$ clusters at 956 cm^{-1}. 12M1 indicates $Fe_{12}(CH_3OH)$, 7M2 indicates $Fe_7(CD_3OH)_2$.

As expected, for clusters with one methanol increasing fluence decreases survival probability, possibly showing evidence of saturation at high fluence. Interestingly, clusters with two methanol adsorbates do not show as steep a fluence dependence over the fluence range covered which may indicate that saturation occurs at lower fluence than in mono-methanol clusters. While the data is admitedly sparse, the range of systems which may be studied and the questions which may be asked are tantalizing, indeed.

Conclusions

Infrared multiple photon chemistry continues to be a fascinating area of research. New lasers covering broader regions of the infrared spectrum are allowing a clearer picture of the IRMPE process and concommitantly the nature and couplings of excited molecular vibrational states. IRMPE is becoming a generally applicable research tool for reaction kinetics and dynamics, and spectroscopy. This acceptance is coming about through an increased ability to control IRMPE and through the availability of new, direct probes of reaction intermediates. The emergence of IRMPE as a controlled excitation source to produce selected intermediates, generate homogeneous high temperature reaction zones and probe the vibrational spectroscopy of transient species gives infrared laser chemistry a unique position in the chemist's toolbox.

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