TUNABLE ULTRAVIOLET LASER STUDIES OF PHOTON–MOLECULAR INTERACTIONS OF COMETARY INTEREST

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ABSTRACT. Most of the cometary radicals are thought to be formed in the coma by photodissociation processes. Successful modeling of the coma requires a detailed knowledge of the products that are formed from the various parent molecules, and the energy partitioning among these products. This information has to be obtained as a function of wavelength, because the Sun is not a monochromatic source. In this review, the status of the experimental knowledge of some key molecules will be discussed, along with the prospects of some new laboratory techniques that can fill in the gaps in our present knowledge.

INTRODUCTION

The ultimate goal of cometary science is to determine the parent molecules of the observed cometary radicals. This information will allow us to ascertain if comets are really frozen samples of the primordial solar nebula. Since the observed radicals are known, laboratory information can be used to identify their possible parents.
     Radio observations of comets have identified H_2O [1,2], NH_3 [2], HCN [3], and CH_3CN [4] in comets. All of the photodissociation and photoionization products from water have been found in the coma. Some of the expected photodissociation products of the other molecules have also been observed. With the advent of space missions to comets it is likely that new parent and daughter molecules will be discovered in the coma. It is important to develop laboratory techniques to obtain the photochemical information needed for modeling the observed cometary phenomena.
     The identity and energy content of all of the products of the photon–molecular interactions are needed by the cometary scientist. Both of these are a function of the energy of the photon. For a polychromatic source like the Sun, the laboratory information has to be obtained at many wavelengths. This can be a formidable task because of the difficulty of obtaining the necessary information at even one wavelength. Fortunately, the process can be simplified, if the solar spectra is convoluted with the absorption spectra of the molecule under

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investigation. Those spectral regions with the most overlap will be
the most important regions to investigate in the laboratory. The par-
tial dissociation fraction, P_f, can be defined as the ratio of the
dissociation probability in a given spectral region divided by the total
dissociation probability.

Table I summarizes the partial dissociation fractions for a number
of parent molecules that have been observed in comets. This table
shows that the Lyman alpha is an important region for a number of mole-
cules and that molecules with even a weak absorption at longer wave-
lengths will have large dissociation fractions because of the solar
radiation distribution.

The grid that is chosen for calculating the partial dissociating
fraction is important. It should be at least as small as the corre-
sponding grid for the photodissociation cross section. This is not
necessarily the same as the resolution needed for a particular absorp-
tion spectra because of several factors. If over a given wavelength
region, it can be established that the photochemical products are un-
changed, then a coarse grid describing these products may be used even
though the absorption spectrum may be finer. We have observed, in some
cases, that even if the absorption spectrum of the molecule is continu-
ous the nature of the products can change requiring a finer grid for
the partial dissociation fraction. This is clearly indicated in Fig. 1
where the results of "Laser Induced Fluorescence," i.e., LIF, studies
of the CN radical show that there is a dramatic change in the energy
partitioning in the photochemical fragment with changes in wavelength.
The vibrational content of the radical _increases_ with _decreasing_ wave-
length, which is counter intuitive to what would be expected.

Intense tunable light sources in the vacuum ultraviolet (VUV)
region are needed to obtain accurate photochemical information in the
laboratory. Recent developments [5,6,7] in laser science suggest that
this goal is now attainable. In the balance of this paper the photo-
chemistry of some key molecules will be discussed and particular
emphasis will be placed upon the gaps in our knowledge about these
molecules.

WATER, H_2O

This is the most important molecule in comets, but even it's photochem-
istry is not completely understood. The most important dissociation
region for comets is the first continuum (185 to 145 nm) where approxi-
mately 83% of the water molecules will be dissociated. Lyman alpha at
121.6 nm will account for most of the balance of the dissociation, i.e.
about 16%. Broadband flash photolysis studies have suggested that most
of the OH radicals are produced rotationally and vibrationally cool.
Laser studies at 157 nm also suggest ground OH radicals are produced
which are rotationally and vibrationally cool so that most of the ex-
cess available energy appears in translational recoil motion. More
detailed studies are needed however to insure that there are no wave-
length regions in the first continuum where the above conclusions are
not true. For example, it could be that vibrationally excited OH radi-

cals are produced at higher rather than lower wavelengths, a result that would be relatively more important in comets than in the laboratory. A preferential population of the upper levels of lambda doublet of the $^2\Pi_{3/2}$ state is also observed at 157 nm. This result could have a profound effect in the optical pumping of the OH radical in comets and the amount of this preferential population should be investigated throughout the first continuum.

The principle dissociation processes at 121.6 nm produce 73% of the OH X($^2\Pi$) state and A($^2\Sigma$) with quantum yields of 0.73 and 0.05 respectively. The quantum yield for $H_2 + O(^1D)$ formation is 0.10, and it is 0.12 for the formation of $2H + O(^3P)$. The internal energy distribution of the A($^2\Sigma$) of OH is very well understood but no satisfactory measurements have been made for the ground state radicals which make up the principle dissociation channel. These measurements will require sensitive laser techniques in this wavelength region.

CN PRODUCTION

Until recently it was generally agreed that HCN was the principle source of CN in comets [8]. Crovisier and Bockelée-Morvan have suggested that there are other significant sources of CN in comets because of the lower upper limit of the HCN production rate that could be derived from radio observations of comets IRAS-Araki-Alcock 1983d and Sugano-Saigusa-Fujikawa 1983e [9,10]. They have suggested C_2N_2 and HC_3N as this additional source of CN. Table I shows that Lyman alpha is an important photolysis region for both of these molecules. Of the three molecules, the C_2N_2 photochemistry is the best understood [1,11, 12]. Most of our understanding of the photochemistry of these molecules is in the 150 to 200 nm region. Despite this, quantum yield measurements, and energy partitioning measurements of the ground state CN fragment are still needed at wavelengths below 150 nm for this and other molecules. To do this accurately, intense light sources in this region are needed as well as a computer automated data collection system, because laser sources will have large pulse to pulse intensity variations which must be corrected for on a pulse to pulse basis.

CS PRODUCTION

The CS emission in comets is one of the most prominent emissions observed in the IUE spectra of comets. It is extremely important since it is concentrated near the nucleus of the comet where collisions are still occurring. Its spectra offers a means of remotely probing this region of the coma. The most likely source of CS is the photodissociation of CS_2, which occurs with a high quantum yield in the 185 to 220 nm region. Other possibilities are the HNCS and the H_2CS molecules. In the former case, it has been shown that for wavelengths > 190 nm, the primary processes lead to the formation of the HNC and NCS radicals [13], so it is unlikely that significant amounts of CS are produced from HNCS. Little can be said about H_2CS since this molecule is unsta-

ble at room temperature, but arguments have been presented that suggest that this is not the major source of CS [14].

The photodissociation of CS_2 illustrates some of the problems encountered by laboratory scientists in obtaining all of the information needed for cometary science. The molecule has been extensively studied at 193 nm and the work up to June of 1985 has been reviewed [12]. At this wavelength there is about 2 ev of excess energy that must be divided between the photochemical fragments. Some of this energy can be used to electronically excite the S atom. It can also appear as either internal energy in the CS radical or translational recoil energy. Recent work, since this review suggest that the $S(^3P)$ is the primary atomic product. Laser diode IR studies have shown that the CS radicals are produced with rotational energies up to $J'' = 100$. New LIF studies confirm that the vibrational distribution of CS extends up to $v'' = 12$, the rotational distribution is hot, and the rotational line is broadened by Doppler broadening. All of this complexity is observed at "one" wavelength and a similar complexity can be expected at other wavelengths that are important to cometary science. It will probably be a while before definitive laboratory results are available for this molecule.

THE C_2 PROBLEM ?

One of the most puzzling problems in cometary science is the origin of C_2 in comets. Over ten years ago [8], the present author suggested that C_2 was produced by the secondary photolysis of C_2H. The C_2H radical was produced by the photolysis of C_2H_2 in the low pressure environment present in comets. In the laboratory the radical reacts rapidly with the acetylene molecule which can lead to rapid polymerization in the system. The problems with quantifying this suggestion are, little is known about the absorption spectra of the C_2H radical and it is difficult to build up high concentrations of this radical. Attempts have been made to determine the absorption spectra of the free radicals by using a multi-laser experiment. Neither the intensity of the available lasers nor their stability was high enough to accomplish this goal. Theoretical calculations suggest that C_2H radicals, in the lowest vibrational and rotational levels, cannot lead to the observed C_2 by a one photon transition. Despite these theoretical calculations, there is recent laboratory evidence [15] which proves that the C_2 radical can be produced by the secondary photolysis of C_2H. This coupled with the analysis of cometary observations [16,17], which indicate that the C_2 radical is a grand-daughter radical, is strong support for the original claims that this radical is produced by the sequential photolysis of C_2H_2. Yet, it is troubling that the theoretical results could be so wrong. The answer to this dilemma may lie in the energy partitioning among the photochemical fragments. If a large amount of the excess available energy appears as internal energy of the C_2H radical this could aid the overall dissociation process. The truth awaits more definitive laboratory experiments and theoretical work.

SUMMARY

Laboratory photochemical data has played a crucial role in our under-
standing of observed cometary phenomena. While a good deal is known
about photodissociation process of parent cometary molecules there are
still significant gaps in our knowledge. Present experimental tech-
niques appear to be able to clear up some of these gaps and this cou-
pled with more theoretical results should eliminate a lot of the
present problems. Despite these advances, it is likely that results
that will be obtained from cometary missions and observations of Halley
will uncover new problems to challenge both experimentalist and theo-
rist.

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TABLE 1. Fractional Dissociation Probability, $P_f(\lambda_1 - \lambda_2)$ and Photochemical Lifetime, t_T, of Parent Precursor Molecules

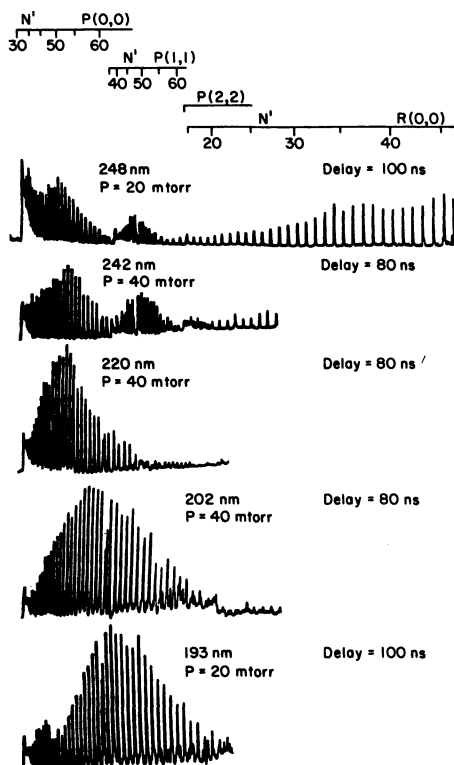| Parent Molecule	Daughters	P_f Wavelength Region (nm)				$t_T(s)$ Total Lifetime
		100–150	121.6	150–200	> 200	
HCN	CN; H	0.05	0.81	0.14	–	9×10^4
$C_2\hat{N}_2$	CN	0.14	0.69	0.16		1.1×10^4
CH_3CN	H; CH_3; CN; CH_2CN	0.49	0.51			6.7×10^5
HC_2CN	HC_2; CN	0.11	0.17	0.72		1.3×10^4
NH_3	H; NH_2	0.09	0.012	0.16	0.82	2×10^3
C_2H_2	H; C_2H; C_2(?)	0.004	0.17	0.83		5.7×10^3
H_2CO	H; HCO; CO; H_2	0.008		0.17	0.82	1.9×10^3
CS_2	CS; S				100 (190–220)	6×10^2

Figure 1. Note that the relative vibrational population increases with decreasing available energy.

DISCUSSION

NEUFELD: What are the prospects of making measurements shortwards
of 100nm? The reason I ask is that some cometary molecules may be
photodissociated predominantly by Lyman continuum radiation. An
example will be CN, according to the theoretical cross-sections of
Lavendy et al.
JACKSON: Non-linear third harmonic generation has been used to obtain
laser radiation in this wavelength region. The experiments may be
difficult, because beam experiments may be required since this wave-
length does not propagate through most windows and gases.

GREENBERG: You did not suggest OCS as a possible parent molecule for
CS in comets. OCS is seen in the dust in W33A and is also produced by
photoprocessing of ices containing H_2S. Thus it is likely to be a
parent molecule in comets. Is the reason you did not consider OCS as
a source of CS that it is much more likely (and this is energetically
strongly suggested) to photodissociate into CO and S rather than CS
and O?
JACKSON: The laboratory results suggest that OCS photodissociates to
yield CO + S.

YAMAMOTO: You showed N_2H_4 is a parent molecule that produces NH. Do
you have any idea about the lifetime of N_2H_4 against photodissociation?
JACKSON: I do not have this molecule in the table I have shown. I
think I have calculated it using data above 200 nm and I will include
it in the final version of my paper.

MITRA: Do you have problem with the stability of lasers in the
vacuum UV region? What is the maximum variation from pulse to pulse?
JACKSON: There is a great deal of pulse to pulse variation in the
VUV output of these lasers. VUV lasers are obtained by non-linear
mixing schemes which will amplify any original variation in the
fundamental visible or near UV output of the laser. To compensate
for this we normalize all signals on a pulse to pulse basis.

P.A. FELDMAN: In the photoionization and photodissociation of cometary
NH_3, how likely is it that NH_3^+ will be produced?
JACKSON: I think that NH_3 has a fairly low ionization potential of
the order of 10 eV. If this is true then it will be photoionized
fairly efficiently.