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HIGH RESOLUTION SPECTROSCOPY : NEW MOLECULES NEW METHODS

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Till recently, molecular structural studies by high resolution spectroscopy have been limited to molecules which have a relatively long life and which could be obtained in reasonably large quantities. Many systems like molecular ions, van der Waals molecules, clusters, interstellar species, plasma components, reactive intermediates, weakly bonded complexes etc. could not be studied by conventional high resolution spectroscopy. With the advent of a variety of fixed frequency and tunable lasers, several new methods were developed which could be used for high resolution spectral studies. Thus methods like laser stark spectroscopy, laser magnetic resonance, infrared-microwave double resonance, two-photon spectroscopy, and Doppler-tuned ion spectroscopy have come into existence. Techniques like supersonic molecular beam spectroscopy, intracavity laser stark spectroscopy, Magnetic field modulated laser spectroscopy, velocity modulation spectroscopy and laser optogalvanic spectroscopy can now be routinely applied for high resolution spectral studies of new molecular species which may be present or which could be produced at trace levels in electric discharges, supersonic beams, chemical reactions, photophysical processes etc. Some of the experimental techniques and results on typical systems will be reviewed in this paper.

Key Words : High Resolution Spectroscopy; Molecular Ions; Clusters

INTRODUCTION

HIGH resolution spectroscopy has always been the standard method for structural studies of free molecules. Till recently, such studies have been mainly restricted to stable molecules. However, in such diverse fields as chemical kinetics, photochemistry, laser physics, astrophysics and molecular dynamics from which a host of information could be obtained on structure, intermolecular interactions, primary chemical events, collision physics etc., the technique of high resolution spectroscopy could not be applied on a wide scale, because the species of interest were often present in only trace amounts, are produced under hostile conditions for spectral studies, and may have very short life times. Recently, with the advent of tunable lasers several new techniques of high resolution spectroscopy have been developed for investigation of such molecules. In this paper we review some of these techniques and their applications.

The systems studied include—molecular ions produced in glow discharges, hollow cathodes, a.c. discharges, ion-molecule reactions etc.; van der Waals molecules produced in supersonic free jet expansions; dimers or clusters present

either in normal monomeric samples, or in supercooled molecular beams; refractory species produced under various conditions; and finally free radicals, reaction intermediates etc. produced by photo-dissociation, electron bombardment etc. Depending on the species produced, the techniques for their studies vary, and below we will consider the more important of these species and the corresponding techniques.

Spectroscopy of Molecular Ions

Chemists have always been familiar with molecular ions like NH_4^+, OH^-, H_3O^+, and many molecular ions, simple and complex, have been detected by mass spectrometry. But till recently, no molecular ion has been studied spectroscopically in its free state to obtain information on structure, energy levels, lifetimes etc. Many of these molecular ions have now been studied through their high resolution spectra.

Molecular ions can be of different type. We can have protonated ions (H_3^+,H_3O^+, NH_4^+), deprotonated ions OH^-, NH_2^-), radical cations (OH^+, NH_3^+), and radical anions (C_2^-). These molecules are produced in ion-molecule reaction, electron bombardment, electrical discharges, photoionisation reaction etc. Almost always only very small amounts of the required species are produced, and they exist in the presence of extremely large amounts of other molecules which may give considerable spectral interference, and this interference has to be eliminated or reduced before the molecular ion spectrum can be obtained.

One of the first polyatomic molecular ion investigated by high resolution infrared spectroscopy is the H_3^+ ion.[1,2] Fortunately, this molecule is produced by a discharge in H_2 in a long copper hollow cathode, and the large amounts of H_2 present give no infrared absorption to interfere. Hence direct absorption method using multiple traversal over path lengths of several meters has been used for spectral studies. The number density of the H_3^+ molecule in these studies was about 3×10^{10}/c.c. ($\sim 10^{-6}$ torr). The study was made possible because of the development of a widely tunable, narrow band, difference frequency laser system,[3] which could cover the 2.2–4.2 μm near infrared region with high resolution, so that the widely spaced H_3^+ lines could be observed with Doppler limited resolution. Both the difference frequency laser and semiconductor diode laser have been used later for further high resolution studies on H_2D^+ and HD_2^+.[4,5]

As we have already mentioned, the direct absorption technique may not be easy to use in the case of many molecular ions because the ions are produced only in small amounts in systems which can have other infrared absorbing neutral species in large amounts. An ingenious method by which this problem can be overcome is the velocity modulation technique.[6] In this technique, the discharge producing the molecular ions is driven with a symmetric bipolar square wave. In such a discharge, the charged molecular ions are Doppler shifted into and out of resonance with the laser as a result of their drift velocities in the plasma which

reverse every half-cycle of the discharge wave form. Neutral species are not affected by polarity reversal. If now laser power is measured with a lock-in amplifier tuned to the modulation frequency, absorption of neutral species is almost completely suppressed and only molecular ion absorption is measured. The discrimination has been found to be better than 10^5. The technique of velocity modulation has been used for studies of several molecular ions like H_3O^+, H_2F^+, $HCNH^+$, NH_4^+, HCO^+, DNN^+ etc.[7-15]

Another method of suppressing the background spectrum and improving the signal to noise ratio is the technique of magnetic field modulation.[16] It has been shown that the production of many positive molecular ions in glow discharges is altered by an order of magnitude or more by the application of a magnetic field[17] (100-500G). If the field is modulated, interference from neutral species can be suppressed by lock-in detection. Molecular ions like HCO^+, CO_2^+, CF^+ and $HCNH^+$ have been studied by this technique using semiconductor diode laser absorption spectroscopy.[18-20]

A very sensitive method in which the splitting of the energy levels of an atom or molecule in a magnetic field is made use of to obtain very high signal to noise ratios in absorption measurements, is the technique of Laser Magnetic Resonance (LMR).[21] In this technique, the principle of electron spin resonance is extended to the infrared region. Coincidence between a molecular transition and the lasser frequency is brought about by magnetic tuning of the Zeeman components and measuring accurately the field required for the transition to take place with a given frequency of the laser. Several molecular species like HCO, OCH_3, C_2H, N_2H, etc. have been studied by this method.[22]

Spectroscopy of Refractory Species, Excimers, Metastables

Molecular ions are not the only molecular species of interest produced in electric discharges. Many refractory molecular species, excimers, metastable species etc. can be produced in the vapour phase by striking an electric discharge in a system cantaining the component elements and a small amount of some rare gas, which sustains the discharge. The technique of laser optogalvanic (LOG) spectroscopy can be used to study neutral and ionic molecular species in such discharges and similar plasmas. A typical LOG set up for use with a CO_2 laser is shown in Fig 1. We have investigated discharges in CO_2, NH_3 etc. by this technique.[23] Molecules like NH_2, CuO, He_2 etc. have been studied by this method.[24-30] The optogalvanic method is especially useful for refractory oxides, and molecules like He_2 with repulsive ground states. Another advantage of LOG is that the spectra can be studied with relatively small amounts of samples, because the method is dependent only on radiation absorbed, and not on measurement of intensity changes due to absorption.

Van der Waals Molecules, Clusters and Related Species

High resolution spectroscopy of molecules whose constituents are held together by weak forces are very important, since the spectroscopic data will give us

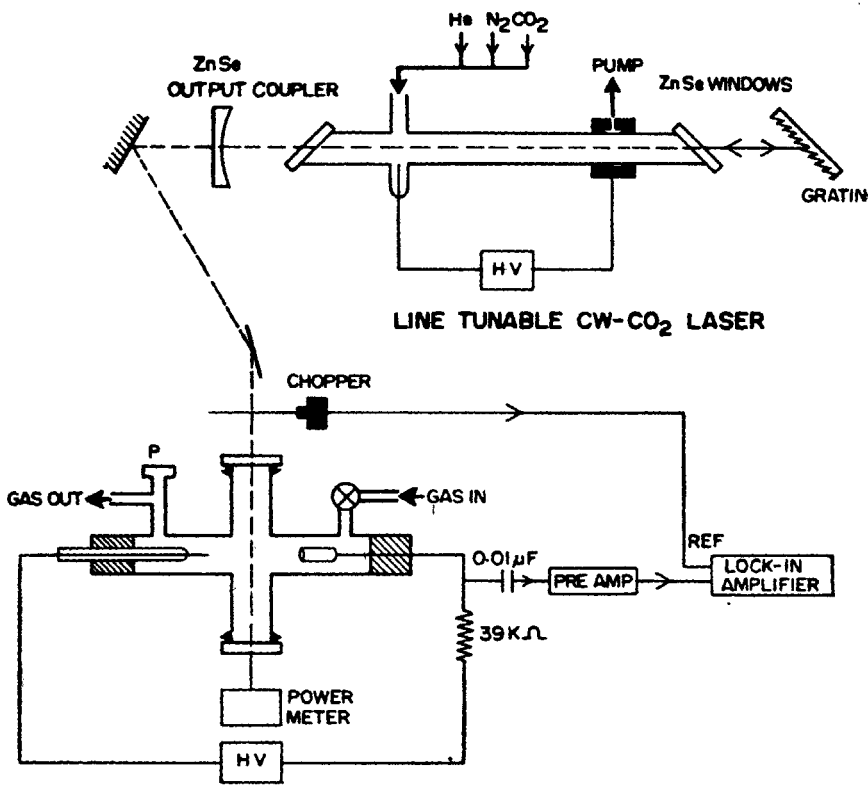

FIG 1 Optogalvanic spectroscopy set up with CO_2 laser.

information on the correct structure of such systems. These structural details will lead to a clear understanding of various phenomena like inter-molecular interaction, chemical dynamics, structure of liquids etc. A large number of van der Waals molecules, clusters and hydrogen-bonded species have been studied very recently by new spectroscopic techniques.

Some of these species, like dimers, could be present in small amounts in the natural sample. A classic example of this is $(HF)_2$. The hydrogen fluoride dimer spectrum comes very near the spectrum of the monomer, and it would have been very difficult to study this by conventional high resolution spectroscopy. But the very high resolution and wide frequency coverage afforded by the difference frequency laser has enabled Pine and coworkers to sort out the dimer spectrum from the overlapping HF spectrum.[31]

In the case of $(HF)_2$, the interaction is sufficiently strong for the dimer to exist at room temperature. But for many van der Waals molecules and clusters, the attractive forces are so weak, that until recently, they have been studied only by matrix isolation techniques at low temperatures.[32] Matrices of even inert solvents may considerably distort the structure of the weakly bonded molecule.

Also the rotational motion for almost all molecules will be frozen in the solid matrices and no information on rotational spectra could be obtained under such conditions. These difficulties can be overcome by forming these molecules in an environment where they will remain stable and free from other interactions, and this can be achieved in supersonic free jet expansion.[33]

In a supersonic nozzle beam, gas at high pressure in one chamber is allowed to expand through a small nozzle orifice into a vacuum chamber, which is pumped by a high speed diffusion pump. The expansion through the nozzle converts the random thermal motion in the high pressure chamber to a directed flow. As a result of this geometrical orientation and the large number of collisions at the exit, the velocities of the molecules become very uniform and the width of the velocity distribution becomes very small, corresponding to very low translational temperatures, of the order of a few K. As a result of the collision, the internal degrees of freedom—that is, the vibrational and rotational energies—also relax toward the

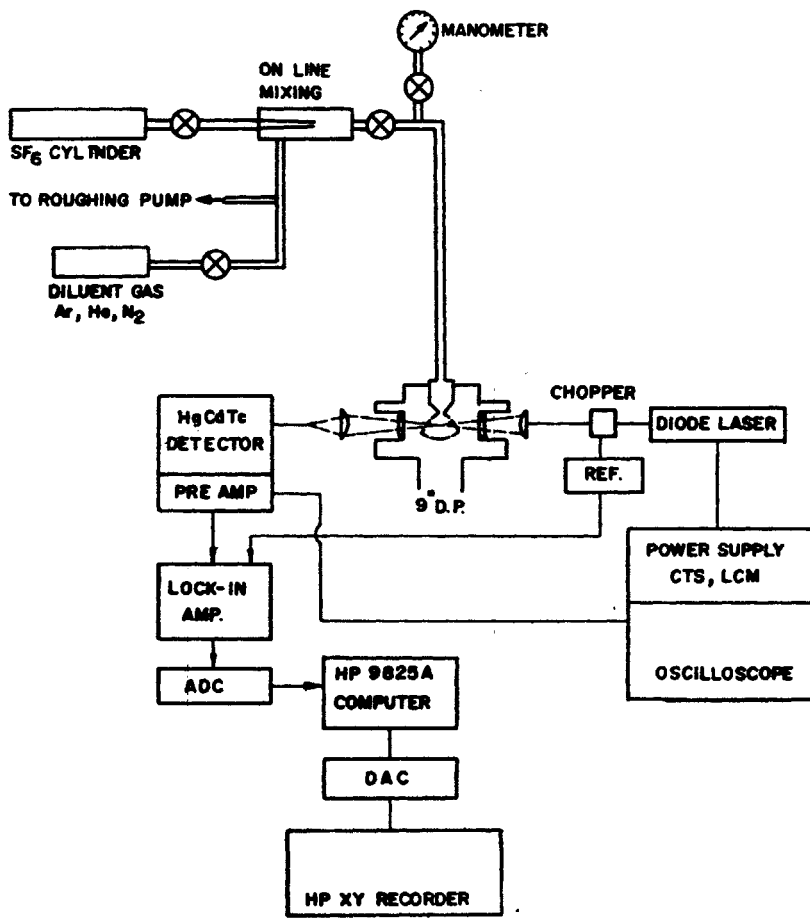

FIG 2 Schematics of system for diode laser absorption studies of supercooled jets.

low temperatures. The extremely low temperature baths associated with such beams provide an ideal environment for generation of the weakly bonded systems under discussion. The supersonic free jet can also be used to prepare and preserve a high concentration of free molecules, ions, radicals, clusters etc. in specified internal states.[34] Spectroscopy of these species, many of which cannot be obtained under normal conditions, can be then carried out by using several new laser spectroscopic techniques. These techniques include, direct absorption, laser-induced fluorescence, laser opto-thermal detection, coherent Anti-Stokes Raman

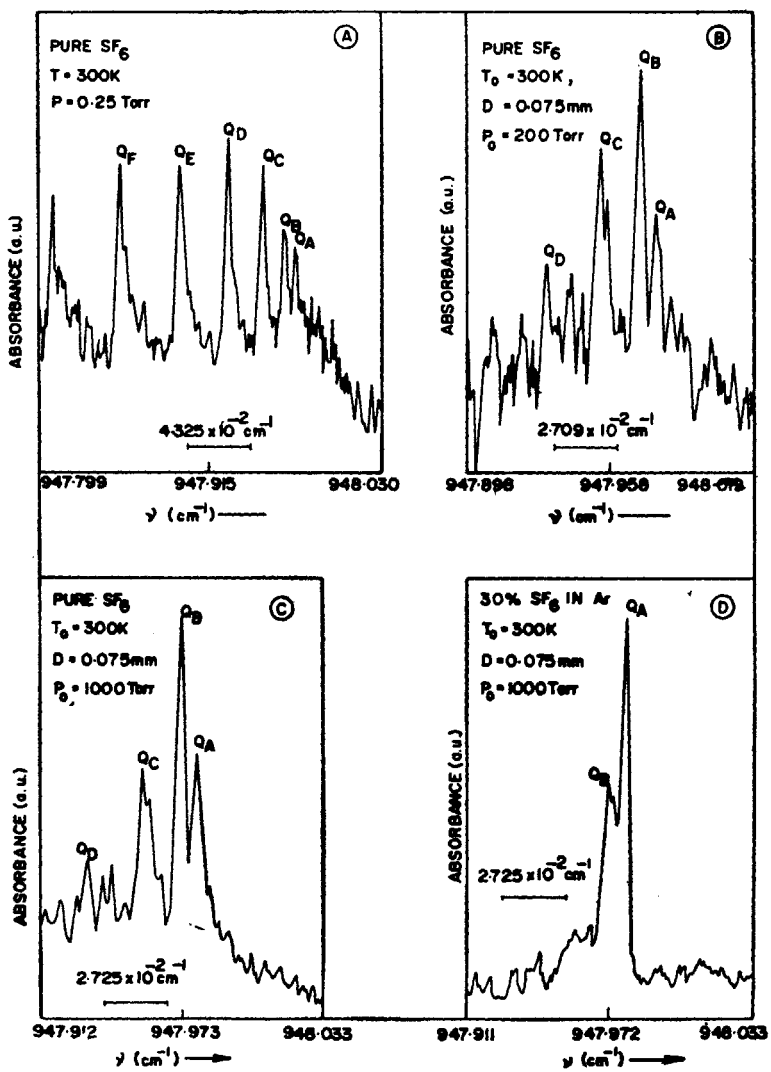

FIG 3 Diode laser absorption spectrum of Q-branch region of SF_6.
A. 0.25 torr in 10 cm cell at room temperature
B,C,D. Absorption spectra of nozzle-cooled SF_6 samples, under conditions shown in the figure. D-Nozzle diameter. P_0-Stagnation pressure

Spectroscopy, Inverse Raman Spectroscopy, Laser Stark Modulation, Two-photon Absorption and ionisation, stimulated Emission pumping etc.[33–53]

A diode laser absorption system with supersonic free jet expansion which we have used in some of our studies, is shown schematically in Fig. 2. A typical series of spectra, illustrating the cooling produced in such systems, is shown in Fig. 3 for SF_6. Here, the series of Q-branch peaks Q_A, Q_B, Q_C., shown in Fig. 3A, for room temperature correspond to formation of band heads at progressively higher and higher J-values, when a large number (upto $J > 100$) of rotational levels are populated. In the spectra shown in Fig. 3 B, C and D, these band heads progressively disappear, due to increased cooling at successively higher pressures, since at the lower temperatures, the higher J levels get depopulated. Finally as shown in Fig. 3 D, only Q_A is seen, corresponding to a rotational temperature of 4K.[36] Recently, the formation of Ammonia clusters have been demonstrated by us[37,54] by diode laser absorption, and their spectra have been observed by CARS.[46]

The supersonic free jet can also be used to produce *in situ* new molecular species, chemical intermediates, free radicals, molecular ions etc. by photochemical reaction, electron impact ionisation, corona discharge, chemical reaction etc.[34]

In conclusion, there is no limit to the number and variety of new molecular species that can now be studied by the new and extremely sensitive laser spectroscopy techniques. The high resolution spectral data obtained from such studies will provide valuable information on inter and intramolecular interaction, structural parameters, reaction pathways and mechanisms, molecules of astrophysical importance, fundamental chemical aspects etc.

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