

Thermal detection laser spectroscopy of molecular beams

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Abstract. We describe the experimental methods used in carrying out high resolution infrared spectroscopy of molecular beams using bolometric thermal detection. The main applications of this technique are also described and include: studies on molecular internal vibrational relaxation, radiationless transition after “visible” excitation, photodissociation spectroscopy of van der Waals molecules, the study of coherent excitation of molecules in the infrared, multiphoton infrared spectroscopy, overtone spectroscopy and the study of large molecular clusters.

Keywords. Thermal detection laser spectroscopy; molecular beams; bolometric thermal detection; high resolution IR spectroscopy.

1. Experimental methods

There are several reasons why it is useful to carry out infrared spectroscopy on molecules in a molecular beam environment. These are: (a) the spectral simplification which is due to the cooling of the molecule in the free jet expansion at the supersonic beam source, (b) the high level of resolution achievable by crossing the molecular and the laser beams at right angles to each other eliminating first order Doppler broadening of the spectral lines, (c) the possibility offered by the beam environment of producing and using unstable species such as van der Waals molecules and free radicals, (d) the possibility of using very high external fields, which is due to the smallness of the interaction volume ($\sim 1 \text{ mm}^3$) and the presence of vacuum conditions that reduce chances for electrical breakdown, and, last but not least, (e) the absence of collisions, which can be reintroduced, if desired, by intercepting the molecular beam with a secondary crossed beam or with a surface.

Two main experimental methods are presently used which account for most of the results at the highest resolution levels. One can either monitor the modulated absorption of a laser beam occurring when crossing the flux emerging from a pulsed linear jet (Lovejoy and Nesbitt 1987) or measure the energy deposited by the laser in the molecules of the beam, using microcalorimetric methods, i.e. using a low temperature bolometer detector located downstream from the laser crossing (Gough *et al* 1977; Miller 1986). The first method requires a tunable laser of high stability but makes no particular demands on its power level. The maximum resolution achievable is of the order of 30–50 MHz and is limited by Doppler broadening still present in the expansion at the point where the laser is sent across it (i.e. at the best compromise point between resolution and column density). With this method absorptions between 10^{-5} and 10^{-6} have been detected. The second method, often called the photothermal detection method, does not have particular requirements on

the laser source stability, provides higher resolution (3–5 MHz, limited by residual Doppler broadening) but, in analogy with photoacoustic methods, requires relatively powerful and tunable laser sources. However, when these are available, such as in the region of $1.5\ \mu\text{m}$ (color center lasers) and in the region of $10\ \mu\text{m}$ (CO_2 lasers), experiments become possible, such as the measurement of overtone spectra, which are much more difficult (if not impossible) using absorption techniques (Meyer *et al* 1989).

Soon after the introduction of photothermal detection, it became apparent that the

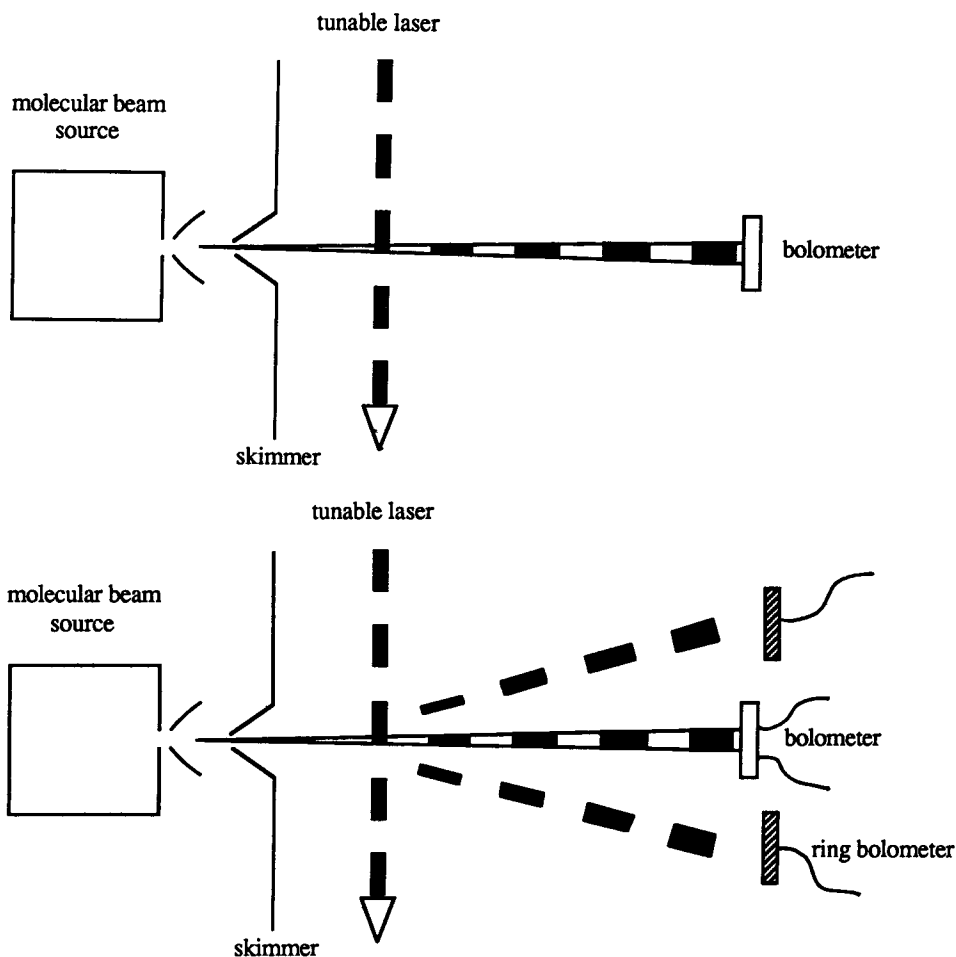


Figure 1. The two basic experimental schemes of photothermal detection spectroscopy. The arrangement at the top shows an amplitude modulated laser tuned to be in resonance with a molecular transition inducing a modulation in the energy contents of an unmodulated molecular beam which is detected by the bolometer located downstream from the excitation point. Frequency modulation of the laser is also possible of course. The arrangement at the bottom shows an amplitude modulated laser (tuned to be in resonance with a molecular transition) inducing, by photodissociation, a modulation in the number of molecules present in the beam (and therefore also an energy modulation). The fragment flux can of course also be detected with a bolometer located outside of the main beam flux.

method could equally well be employed to monitor the loss of beam intensity produced by the laser in the course of any resonant photodissociating transitions of the beam molecules (Gough *et al* 1978). While the first application of this technique was carried out with bolometric detection, similar results can, of course, be obtained using mass spectrometry based detection techniques (Celii and Janda 1986). Furthermore, two modes of operation are clearly possible. The first consists in detecting the beam depletion by means of an on-beam detector (Gough *et al* 1978) while the second makes use of off-beam detection to monitor the flux due to the photofragments (Gough *et al* 1986) (see figure 1).

2. Spectroscopy of stable molecules

2.1 Exploiting beam collimation and manipulation possibilities

As mentioned above, the main advantages of the collimated-beam photothermal technique are the possibility of easily using multiple laser crossings, homogeneous Stark fields of high intensity and other beam manipulation techniques. For examples we can refer the reader to the detection of coherence effects such as Rabi oscillations (Adam *et al* 1985) and Ramsey fringes (Adam *et al* 1986) and to the measurement of the Stark spectrum for a *non-polar* molecule (CO_2) carried out in the author's laboratory (Gough *et al* 1983b; Cai *et al* 1987). Intracavity excitation with a CO_2 laser has also been used to monitor single-mode, c.w., multiphoton excitation of beams of SF_6 (Liedenbaum *et al* 1988). In this way a very high percentage of the beam molecules can be pumped up to the $v = 5$ level (the anharmonic bottleneck) while a second red-shifted laser can easily pump the molecules to a much higher vibrational state.

2.2 Visible and UV spectroscopy

In the visible and UV region of the spectrum photothermal detection is, of course, complementary to fluorescence and phosphorescence detection techniques. When these techniques are present in the same apparatus a complete energy balance is obtained since the energy that leaks into the "bath" modes via radiationless transition can also be monitored. In this way energy redistribution and radiationless transitions can be studied with unprecedented detail (van Herpen *et al* 1988). Also in the visible the availability of powerful tunable sources in combination with the use of a power build-up cavity has allowed the measurement of overtone spectra in the region of the high ($v = 4$ or 5) overtones (Douketis *et al* 1985). So far, this has been possible, however, only for relatively small molecules.

2.3 Intramolecular vibrational relaxation

Because of the high resolution that can be achieved, molecular beam spectroscopy allows the possibility of measuring single quantum level spectra, resolving the splittings due to the perturbations caused by the background states when the density of these is sufficiently high. Using these techniques the coupling between intramolecular dynamics and stationary states can be studied using both fundamental and overtone

molecular vibrations. For instance, recently we have observed that the overtone of propyne and the trifluoropropyne fundamental, which have transitions in regions of comparable density of states, have very similar spectra. Both show a mixture of unperturbed and perturbed subbands in the parallel band spectrum. The perturbations in both spectra are very weak and involve mixings with dark background states with typical matrix elements of 0.01 cm^{-1} indicating high order couplings. In the analysis of the ν_1 fundamental of CF_3CCH (Lehmann *et al* 1990) we have shown that the dominant interaction is from an anharmonic resonance with a single background state and is *not* due to Coriolis coupling.

This type of work is typical of the field of intramolecular vibrational relaxation (IVR) which has been a subject of considerable interest to the chemical physics community for quite some time.

High resolution studies have shown that at high level densities, large numbers of individual perturbations are typically found in the rovibrational spectrum. Often the eigenstate density observed in the spectra exceeds the estimates of the total vibrational density of states calculated using known anharmonicities. The true statistical limit is expected when the mean level spacing of coupled levels is much less than the mean coupling matrix element. Standard statistical models predict a Lorentzian lineshape in this limit, but, up to the present time, this has not been confirmed experimentally. A Lorentzian lineshape corresponds to exponential decay of the dipole correlation function as one expects for a true 'relaxation' process. The difficulty has been that in situations where this 'homogeneous' broadening of the lines may exist, such as the visible overtone bands of benzene (Page *et al* 1988), the unresolved rotational structure has prevented unambiguous separation of the homogeneous lineshape, which is directly related to the intramolecular dynamics, from the inhomogeneous components.

We have recently measured the molecular beam spectrum of $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{H}$ and $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$ by exciting their acetylenic CH stretching fundamental vibration. Very different behaviour is observed in the two spectra. For $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{CH}$, each transition has a Lorentzian lineshape with a linewidth of 800 MHz FWHM independent of J within the limits of our measurements (from $J = 3$ to 19). The only possible interpretation of the spectrum is that the $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{CH}$ is showing true homogeneous broadening due to statistical IVR with a lifetime of 400 ps. It is certainly true that each 'line' is made up of transitions from a collection of K and internal rotor states in the ground state. But the splittings expected for both these inhomogeneous effects should increase at least quadratically with J . We have, therefore, concluded that this is the first clear observation of a Lorentzian broadened lineshape due to IVR alone. The spectrum of $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{CH}$ represents a surprise. The lineshape and linewidth of the observed features change irregularly from one J line to another (from about 120 MHz to 180 MHz across the R branch from $J = 4$ to 25), with some partially resolved structure and clear asymmetry. We may state with confidence that the 'homogeneous' lifetime (if it has one) is $> 2 \text{ ns}$ and thus is at least a factor of 5 longer than for *t*-butyl acetylene. A possible explanation for this effect is that the heavier mass of the Si is blocking the vibrational energy transfer from the acetylenic stretch to the methyl groups whose modes account for most of the density of states (Lederman *et al* 1989; Uzer and Hynes 1989). We see that a factor of 2.3 increase in mass has produced a greater than 5 reduction in relaxation rate, in spite of a substantially higher density of states. Another possible explanation is that the change in mass and force constant has changed the vibrational frequencies, moving

some key "doorway" state out of resonance with the acetylenic stretch. A preliminary account of this work carried out in cooperation with K K Lehmann and B H Pate is in press in the *Journal of Chemical Physics*.

3. Photodissociation spectroscopy

3.1 *Small van der Waals clusters*

Using the technique described in §1 during the last five or six years the IR photodissociation spectra of many van der Waals molecules have been measured. Typical examples in the 10 μm region of the spectrum, which is available due to the existence of line tunable CO_2 lasers, are $(\text{SF}_6)_2$ (Gough *et al* 1986) and $(\text{C}_2\text{H}_4)_2$ (Heijmen *et al* 1987). These spectra have not been rotationally resolved because of the lack of continuously tunable sources in this region (Casassa *et al* 1984). Since rotational resolution is not achieved, these types of experiments suffer also from difficulties vis a vis species identification, especially if the species of interest are trimers or higher oligomers instead of dimers. These difficulties have been solved by Buck and coworkers who identify the different species by their angular distribution after a scattering event and take spectra detecting only a small angular fraction of the beam which has been dispersed by another beam crossing the first at right angles just before or after the laser interaction region (Buck *et al* 1990).

In the 3 μm region literally dozens of systems have been rotationally resolved using either color center lasers in conjunction with bolometric detection (Miller 1988; Fraser and Pine 1989) or difference frequency and diode lasers in conjunction with jet absorption techniques (Matsumoto *et al* 1989; Wang *et al* 1989; Sharpe *et al* 1990; Randall *et al* 1990). In the 1.5 μm (overtone) region instead the only system rotationally resolved so far is the HCN dimer (Meyer *et al* 1989). At the other end of the spectrum, in the far infrared, it has recently been shown that direct access of the van der Waals bond stretching and bending modes is possible (Cohen *et al* 1990).

In favorable cases, when transition dipole moments are large and the lasers powerful, it is possible, using an off-beam rotating bolometer (or a rotating primary beam source), to measure the angular distribution of the photofragments achieving, as in the case of the HF dimer (Dayton *et al* 1989), the full state-to-state selection of the photodissociating channel. A great deal of further work on van der Waals molecules has been carried out, using microwave, Fourier transform (for both IR and microwave) and pulsed laser techniques but its review falls outside of the scope of the present, short, paper. However it is appropriate to remark that, at present, using spectroscopic techniques, enormously detailed information is being gathered on intermolecular forces revealing a great deal about their angular dependence and, via the spectroscopy of trimers and other oligomers, we are also reaching "spectroscopic" precision in the study of non-additivity effects.

3.2 *Large van der Waals clusters: solvation studies*

Experiments with larger clusters do not provide an equally detailed structural picture and, therefore, they provide little quantitative information on interaction potentials. However, if one assumes the interactions to be well-known (and in several cases they

are) one can derive, from such experiments, a much better understanding of the properties of matter in systems of finite size and of the transition between molecular and bulk behavior in condensed systems. Using clusters where SF_6 is solvated in argon, we have studied the analogies and differences between these cluster-matrix spectra and the solid-matrix spectra measurable with standard techniques (Gough *et al* 1983a). Similar work has been carried out by us (Levandier *et al* 1988) and Janda and others (Celii and Janda 1988) on CH_3F also solvated in argon. The solvated SF_6/Ar clusters are produced in the free jet expansion of a very dilute (< 1 part in 10^3) SF_6/Ar mixture. If, instead, large, *pure* argon clusters are produced and the cluster beam is crossed with a side flux of SF_6 molecules [the pick-up cluster preparation method (Gough *et al* 1985)] spectra are obtained of the chromophore molecule when sitting on the cluster's surface. Using SF_6 , SiF_4 and other chromophores, recently, in our laboratory, we have determined the conditions under which an impurity molecule decides either to solvate or remain on the cluster surface (or be expelled by the clusters if initially solvated in it) (Gu *et al* to be published in *J. Chem. Phys.*). The results have been interpreted and rationalized by Garzón *et al* (1989) and by Amar and Perera (to be published in *J. Chem. Phys.*) using computer simulation techniques.

3.3 Large van der Waals clusters: Dimerization reactions

If, instead of a single chromophore impurity, a second molecule is co-solvated in the cluster, the spectroscopic effects of the eventual complexation reaction of the two solvated molecules can be detected. Using co-expanded $\text{CH}_3\text{F}/\text{Ar}$ clusters and pick-up addition of HCl the complexation reaction between these two species (CH_3F and HCl) has been studied as a function of cluster size (Levandier *et al* 1988) and has been found to proceed to completion within the few tens of μs spent by the cluster flying between the pick-up point and the laser interrogation point. For molecules such as CF_3Cl which, for large clusters remain on the cluster surface (in contrast to CH_3F which solvates for all cluster sizes), the possibility exists, and has been exploited (Levandier D J *et al* to be published in *J. Chem. Soc. Faraday Trans.*) of carrying out the complexation reaction on the cluster's surface instead of in its interior. These experiments provide information on the state of relative mobility of the host and guest molecules in the cluster and, indirectly, on the cluster structure and properties.

The examples given above show the broad range of experiments that have been made possible by the coupling of supersonic molecular beams with tunable narrow band laser sources and the strong impact that such experiments are having on the fields of chemical dynamics and molecular spectroscopy. Given the constant progress of tunable laser sources (especially of the solid state type) we can look forward to several more years of exciting molecular games.

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References

- Adam A G, Gough T E, Isenor N R and Scoles G 1985 *Phys. Rev.* **A33** 1451
Adam A G, Gough T E, Isenor N R, Scoles G and Shelley J 1986 *Phys. Rev.* **A34** 4803
Buck U, Gu X J, Hobein M, Lauenstein Ch and Rudolph A 1990 *J. Chem. Soc. Faraday Trans.* **86** 1923
Cai W Q, Gough T E, Gu X J, Isenor N R and Scoles G 1987 *Phys. Rev.* **A36** 4722
Casassa M P, Western C M and Janda K C 1984 *J. Chem. Phys.* **81** 4950
Celii F and Janda K 1986 *Chem. Rev.* **86** 507
Celii F and Janda K 1988 *Z. Phys.* **D10** 347
Cohen R C, Busarow K L, Lee Y T and Sakally R J 1990 *J. Chem. Phys.* **92** 169
Dayton D C, Jucks K W and Miller R E 1989 *J. Chem. Phys.* **90** 2631
Douketis C, Anex D, Ewing G and Reilly J P 1985 *J. Phys. Chem.* **89** 4173
Fraser G T and Pine A S 1989 *J. Chem. Phys.* **91** 637
Freed K F 1976 *Radiationless processes in molecules and condensed phases* (ed) F K Fong (New York: Springer-Verlag) p. 23
Garzon I L, Long X P, Kawai R and Weare J H 1989 *Chem. Phys. Lett.* **158** 525
Gough T E, Knight D G, Rowntree P A and Scoles G 1986 *J. Phys. Chem.* **90** 4026
Gough T E, Knight D G and Scoles G 1983a *Chem. Phys. Lett.* **97** 155
Gough T E, Mengel M, Rowntree P A and Scoles G 1985 *J. Chem. Phys.* **83** 4958
Gough T E, Miller R E and Scoles G 1977 *Appl. Phys. Lett.* **30** 338
Gough T E, Miller R E and Scoles G 1978 *J. Chem. Phys.* **69** 1588
Gough T E, Orr B J and Scoles G 1983b *J. Mol. Spectrosc.* **99** 143
Heijmen B, Liedenbaum C, Stolte S and Reuss J 1987 *Z. Phys.* **D6** 199
Lederman S M, Lopez V, Fairen V, Voth G A and Marcus R A 1989 *Chem. Phys.* **139** 171
Lehmann K K, Pate B H and Scoles G 1990 *J. Chem. Soc., Faraday Trans.* **86** 2071
Levandier D J, Mengel M, Pursel R, McCombie J and Scoles G 1988 *Z. Phys.* **D10** 337
Liedenbaum C, Stolte S and Reuss J 1988 *Chem. Phys.* **122** 443
Lovejoy C M and Nesbitt D 1987 *J. Chem. Phys.* **86** 3151
Matsumoto Y, Ohshima Y and Takami M 1989 *J. Chem. Phys.* **90** 7017
Meyer H, Kerstel E, Zhuang D and Scoles G 1989 *J. Chem. Phys.* **90** 4623
Miller R E 1986 *J. Phys. Chem.* **90** 3301
Miller R E 1988 *Science* **240** 447
Page R H, Shen Y R and Lee Y T 1988 *J. Chem. Phys.* **88** 4621
Randall R W, Summersgill J P L and Howard B J 1990 *J. Chem. Soc., Faraday Trans.* **86** 1943
Sharpe S W, Zeng Y P, Wittig C and Beaudet R A 1990 *J. Chem. Phys.* **92** 943
Uzer T and Hynes J T 1989 *Chem. Phys.* **139** 163
van Herpen W M, Vijt de Haag P A M and Meerts L W 1988 *J. Chem. Phys.* **89** 3939
Wang Z, Eliades M and Bevan J W 1989 *Chem. Phys. Lett.* **161** 6