Intramolecular vibrational energy redistribution Line broadening

Gad Fischer[a]

[a] GAD FISCHER Department of Chemistry, Ben Gurion University of the Negev, Beer-Sheva, Israel

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by GAD FISCHER

Department of Chemistry, Ben Gurion University of the Negev, Beer-Sheva, Israel

At high vibrational energies the redistribution of vibrational energy is very rapid in accord with the broad linewidths measured. At low energies, no such consistent picture has emerged. For many systems the line-broadening threshold is at about $1500 \, cm^{-1}$, yet for others no broadening is observed for thousands of cm^{-1}. Infrared spectra of ethylene dimers are marked by large linewidths whereas lines narrower by several orders of magnitude are observed for the larger molecular dimers benzene and methylacetylene.

1. Introduction

The success of the RRKM theory of unimolecular reaction rates confirms that the complete or partial randomization of the vibrational energy over the vibrational phase space is much more rapid than other processes, in particular dissociation. For small quantities of vibrational energy, such as are commonly encountered for the lower frequency fundamentals, this is no longer believed to be true and no such rapid randomization takes place. The very small linewidths, less than Doppler, observed in high-resolution IR spectra are evidence of this. Intramolecular vibrational redistribution (IVR) in this sense has its parallel in the phenomenon of electronic relaxation, where for a large energy gap, statistical behaviour is obtained while small-molecule characteristics are noted for a small separation of the electronic states. By further analogy it follows that lineshapes can be non-lorentzian.

IR multiphoton dissociation of polyatomic molecules addressed this question of IVR over the whole range of vibrational energies. To overcome the anharmonicity bottleneck (Ambartzumian and Letokhov 1977) it appears that already with the excitation of a few vibrational quanta IVR must be rapid, although it may not be general but into a specific region of the vibrational phase space.

An important point that arises in all discussions of IVR concerns the extent to which the process is truly intramolecular. Experimentally this raises many constraints and the suspicion nevertheless remains that the neglect of the long-range inter-molecular forces may not be justified.

In parallel with electronic spectra there are many factors that may contribute to an apparent line-broadening. Spectral congestion is an obvious one. We wish to ignore all these so-called trivial factors and restrict ourselves to line-broadening arising from rapid IVR. In this description an initially excited state decays into a dense manifold of iso-energetic states. The individual decay widths, e.g. radiative, overlap so that higher experimental resolution does not lead to separation into a number of lines.

In the normal (or local) mode description vibrational levels that are not necessarily iso-energetic may be coupled (Fermi resonance) so that relative to another electronic state these levels may appear with mixed character. Fluorescence from such a mixed level is characteristic of the levels that are coupled. Clearly, where the excited state has

the mixed-in character of a number of other states the fluorescence spectrum will be very complicated and quite possibly diffuse and lacking in detail. This is a source of broadening in fluorescence spectra we do not wish to consider. It should not be confused with the broadening deriving from IVR. In absorption, intensities and transition frequencies may differ from their predicted values but no broadening is obtained. Spectral congestion may be present.

We now turn to a number of examples that encompass a wide range of vibrational energies. We show that although at high energies there is little disagreement between theory and experiment on the rates, for the low energies a range of behaviours is obtained.

2. High energies

The case of high vibrational energies is very well documented by the elegant chemical activation studies of Rabinovitch and co-workers (Rynbrandt and Rabinovitch 1971, Rabinovitch et al. 1974, Oref and Rabinovitch 1979). One such study concerned the production of hexafluorobicyclopropyl-d_2 activated to about $39\,000\,\text{cm}^{-1}$; rates of approximately $1\,\text{ps}^{-1}$ were measured for the IVR.

The large linewidths observed for the high overtones of the CH stretching vibrations also attest to IVR rates in the ps^{-1} range. The results for benzene demonstrate this. For $v=5$ to $v=7$, widths are obtained from 111 to $90\,\text{cm}^{-1}$ respectively (Reddy et al. 1982) whereas the rotational width determined from the $v=1$ band is only $30\,\text{cm}^{-1}$. Recent work (Buch et al. 1984) suggests that a large part of this width is derived from IVR.

3. Low energies

In the discussion so far no distinction has been made between ground and excited electronic states. Although it is true that excited electronic states are in general separated by much smaller energy gaps than the ground state, and hence the coupling (vibronic) may be more significant, little evidence exists to show any differences in the IVR.

Hopkins et al. (1980, 1983) conducted studies on a series of alkylbenzenes in both ground and excited states. Ring vibrations were excited and their relaxation into the torsions and bends of the alkyl chain was monitored by fluorescence for excitation in S_1 and by laser-induced ionization for indirect excitation in S_0. The broadening of the fluorescence spectra for the molecules with the longer alkyl chains, following excitation of ring modes such as $v_{6b}(530\,\text{cm}^{-1})$ and $v_{12}(933\,\text{cm}^{-1})$, was attributed to sequence bands involving the torsion and bending vibrations. Here the broadening is attributed to spectral congestion but the fact of its occurrence attested to rapid IVR. The observations are reconciled with the fact that the molecules with the longer alkyl chains have larger state densities.

For the occurrence of IVR it is necessary that a sufficient density of states be iso-energetic with the initially excited state. It is largely in this respect that low vibrational energies assume importance. Thus, even for large molecules, provided they are at sufficiently low energies, the threshold density of states may not be attained.

One means of studying IVR has been to measure the linewidths in a progression of spectrally active transitions where for low members the state density is too small to contribute to broadening. This was done in the electronic absorption spectrum of quinoxaline (Fischer 1975) for a progression in the totally symmetric $525\,\text{cm}^{-1}$ mode. For the first three progression members similar linewidths were obtained but for the higher members increased linewidths were recorded.

Although in this case electronic relaxation, in particular inter-system crossing cannot be excluded as the broadening mechanism, a wealth of experimental evidence for vibrational energies in excess of $1500\,cm^{-1}$ suggests IVR as the most likely explanation (Parmenter 1982).

In a similar exercise but involving a progression in a pseudo-localized phonon mode, increasingly larger linewidths were obtained with increasing numbers of quanta (Fischer 1973). The phonons are associated with the low-temperature phosphorescence of diazanaphthyridine in a mixed crystal of durene. The line broadening is attributed to the coupling of the pseudo-localized phonon mode with the quasi-continuum of lattice vibrations. With increasing quanta an increased coupling is obtained, hence explaining the larger broadening in the absence of any significant increase in the effective phonon density of states.

Instead of varying the vibrational energy it is possible to increase the density of states by enlarging the molecule. This was the case in the alkylbenzene work (Hopkins *et al.* 1980).

The formation of molecular clusters in a supersonic beam provides, to a good approximation, a means of obtaining the same initially excited state in both monomer and cluster systems. Hence the same excitation energy is concerned but the densities of states are different and much larger for the latter. The intermolecular bonds are very weak and exercise only a slight perturbation on the monomer vibrations. Nevertheless, in addition to the increase in the density of states arising from the doubling, tripling etc. of the monomer unit, the degrees of freedom associated with the intermolecular bond(s) must also be included. The vibrations associated with the intermolecular bond are of very low relative frequencies and thus conversion of the input vibrational energy solely into the intermolecular degrees of freedom requires very large numbers of quanta. From the theoretical point of view (Beswick and Jortner 1981, Ewing 1982) the most efficient path of IVR requires acceptance of the major part of the vibrational energy by the *intra*molecular vibrations. It follows that at low vibrational energies where the manifold of intramolecular vibrations is both non-uniform and very sparse, wildly erratic and on the average low rates of IVR are predicted.

Until recently this qualitative description stood in marked contrast to most interpretations of the line-broadening in molecular cluster IR spectra. The linewidths measured in the IR predissociation spectra all correspond to IVR lifetimes of about 1 ps and the widths showed a surprising independence of both the nature of the mode excited and the molecule considered (Hoffbauer *et al.* 1983). Ethylene serves as a good example to illustrate these points. Excitation of v_9, the asymmetric CH stretch at about $3100\,cm^{-1}$, with a colour-centre laser (Fischer *et al.* 1983) gave similar linewidths to excitation of v_7, the CH_2 wag at about $950\,cm^{-1}$ with a CO_2 laser (Hoffbauer *et al.* 1983). It should be recognized that no intramolecular accepting modes exist for ethylene below about $820\,cm^{-1}$ yet the IVR rates based on the linewidths are somewhat larger, not smaller, for the latter. In this context it should also be recalled that no broadening due to IVR is seen in the IR spectrum of ethylene monomer.

Recent work (Miller *et al.* 1984) using more dilute mixtures in the preparation of the molecular clusters revealed that for a number of systems the broad bands can be resolved into sets of much narrower components. Of the polyatomic molecules with four or more atoms that have been studied so far, this has been shown to be the case for acetylene (Fischer *et al.* 1985), methylacetylene (Fischer *et al.* 1985) figure 1, and benzene (Fischer, unpublished results of work carried out in the laboratory of R. O. Watts 1984) figure 2. For ethylene (Fischer *et al.* 1983, 1985), dilution did not lead to a
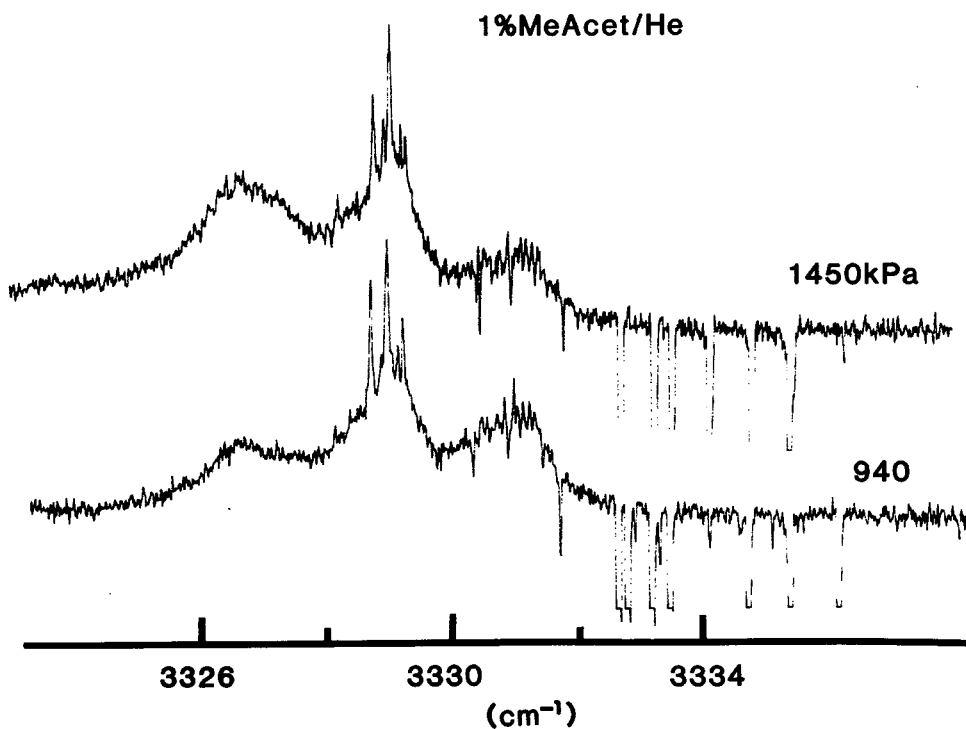
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Figure 1.   The IR (predissociation) spectra of methylacetylene clusters (mainly dimers) in the
region of the acetylenic CH stretch, v_1, at about $3330 \, \text{cm}^{-1}$. The molecular clusters were
produced by expansion of 1 per cent mixtures of methylacetylene in helium at source
pressures of 1450 and 940 kPa. The negative-going signals correspond to monomer
rotational structure.

resolution of v_9 at $3100 \, \text{cm}^{-1}$, suggesting that either the IVR is indeed in the ps^{-1} range
or the spectral congestion is so severe that the right conditions have not yet been found
to ensure resolution into a number of much narrower components.

The interpretations of the line-broadening studies covered in this review are seen to
be ambiguous. In no case is there an absolute certainty that the lineshapes may not be
resolved by the selection of more appropriate conditions. Of course, in some of the
studies considered, particularly those involving excited electronic states, there is the
additional uncertainty concerning the rates of other energy transfer mechanisms, such
as for example electronic relaxation.

There is general agreement that for most polyatomic molecules of four or more
atoms IVR is already in the ps^{-1} range at quite low vibrational energies. Typically the
threshold is about $1500 \, \text{cm}^{-1}$ in both ground and excited electronic states. Neverthe-
less, exceptions exist. The fluorescence spectrum of pyrimidine-d_4 illustrates one
(figure 3) (O'Brien *et al.* 1985). The fluorescence obtained following excitation of the O–
O band may be followed for more than $7000 \, \text{cm}^{-1}$. Although high-resolution
measurements of the linewidths have not been made, the absence of any diffuseness and
the agreement between measured (band heights not areas) and predicted Franck–
Condon factors (O'Brien *et al.* 1985) suggests no line broadening occurs.

BENZENE/He

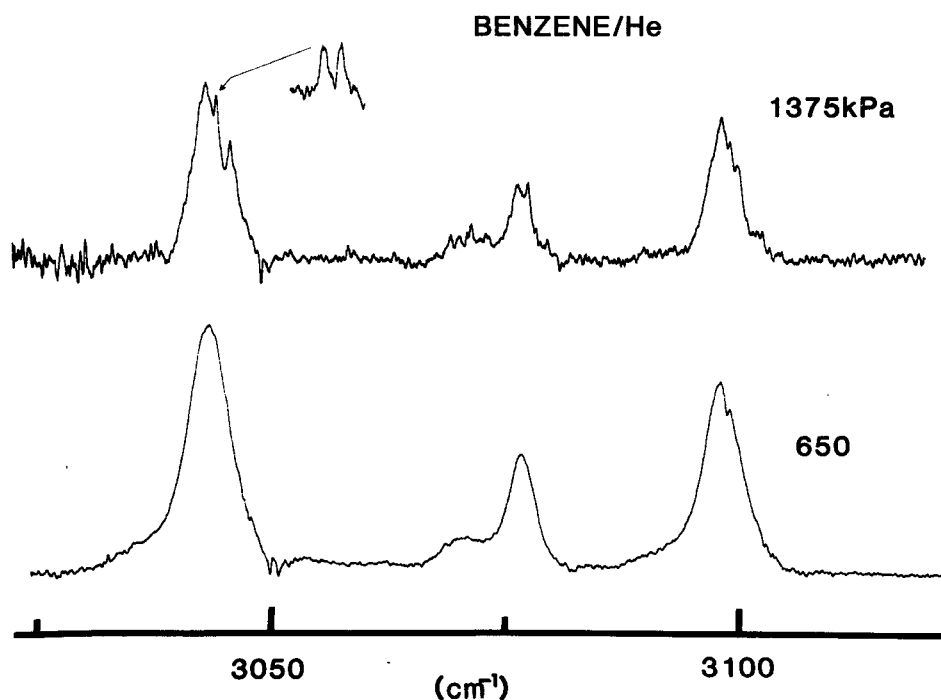**1375kPa**

650

3050 **(cm⁻¹)** **3100**

Figure 2. The IR (predissociation) spectra of benzene clusters at 1375 and 650 kPa source pressures. The doublet separation (shown in inset) is about $0 \cdot 2\,\mathrm{cm}^{-1}$. For benzene vapour only the CH stretch v_{12} absorbs in this region. Combination bands such as $v_{13} + v_{16}$ and $v_2 + v_{13} + v_{18}$ may obtain intensity by Fermi resonance.

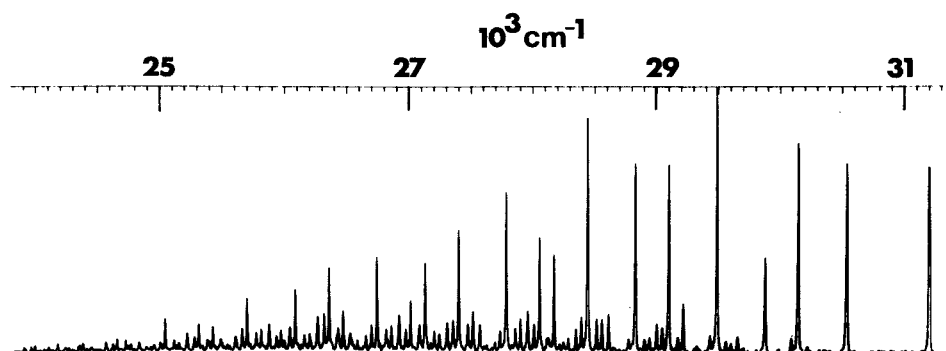$10^3\,\mathrm{cm}^{-1}$

25 **27** **29** **31**

Figure 3. Fluorescence spectrum of pyrimidine-d_4 following narrow band excitation of the O–O band at $31188\,\mathrm{cm}^{-1}$. The spectrum is mainly composed of progressions in $v_{6a}(659\,\mathrm{cm}^{-1})$ and $v_{12}(1048\,\mathrm{cm}^{-1})$. Up to five quanta may be readily identified in each.

It can be concluded that at low vibrational energies the rates of IVR vary over many orders of magnitude in qualitative agreement with theory. However, for larger vibrational energies corresponding to sufficiently large densities of states, IVR rates are in the ps^{-1} range.

Acknowledgment

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