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TILDEN LECTURE*

Overtone Spectroscopy and Unimolecular Reactions

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1 Introduction

Traditional studies of intramolecular dynamics have concentrated either on the low energy (up to 4 000 cm^{-1} or 50 kJ mol^{-1}) normal coordinate vibrational spectrum[1] or on the kinetics of unimolecular dissociation[2-4] at typically 200—400 kJ mol^{-1} or 20 000—30 000 cm^{-1}. The former implies that the energy is permanently locked into one normal mode or the other, while the latter are known to be consistent with the RRKM[3-4] picture of free internal energy flow between all degrees of freedom. The interesting intermediate energy range[5] where one type of behaviour goes over to the other has until recently defied investigation, due primarily to the selection rule $\Delta v = 1$ governing strong vibrational transitions.[6,7]

Various recent spectroscopic advances have begun to overcome this difficulty. One is to employ fourier transform or laser techniques[8-14] which have the sensitivity to detect up to $\Delta v = 9$ transitions in favourable circumstances. Another is to access specific high vibrational levels of the ground state S_0 by energy selective laser excitation to a higher electronic state S_1 which couples back to S_0 by internal conversion.[15-17] The internal states of any decomposition fragments can then be detected by laser-induced fluorescence.[16-17] A third approach is to employ picosecond flash photolysis methods to follow the rate of decomposition in real

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[1] G. Herzberg, 'Infra-red and Raman Spectra', van Nostrand, New York, 1945.
[2] N. B. Slater, 'Theory of Unimolecular Reaction', Cornell University, Ithaca, 1959.
[3] P. J. Robinson and K. A. Holbrook, 'Unimolecular Reactions', Wiley, London, 1972.
[4] W. Forst, 'Theory of Unimolecular Reactions', Academic Press, New York, 1973.
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[13] K. K. Lehman, G. J. Scherer, and W. Klemperer, *J. Chem. Phys.*, 1982, **77**, 2853.
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[17] H. Reisler and C. Wittig, *Ann. Rev. Phys. Chem.*, 1986, **37**, 307.

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time.[18,19] Corresponding information also comes from high resolution spectroscopy of electronically excited states.[20]

This article concentrates on the first method—overtone spectroscopy, which at present implies the spectroscopy of X–H stretching motions, because these are among the few which offer the energy and intensity to access states above 10 000 cm^{-1} (120 kJ mol^{-1}). Section 2 below describes the detailed spectroscopy of very small molecules such as H_2O, CH_4, and C_2H_2 and explains how the bond anharmonicity of the X–H vibrations leads to a transition from 'normal mode' to 'local mode' dynamics.[21–23] The importance of Fermi resonance as a mechanism for energy transfer between different types of mode[6,20,24] is then discussed in Section 3, with particular relevance to the overtone spectra of $CHFCl_2$[25] and benzene.[11,24] The following section shows the sense in which rates of intramolecular vibrational energy transfer may be inferred from the widths of overtone bonds. Finally Section 5 covers experiments on the overtone induced dissociation of H_2O_2[26–27] and its theoretical interpretation.[26,28,29] Conclusions are summarized in Section 6.

2 Local X—H Stretching Vibrations

Henry[2] discovered many years ago that the predominant X—H overtone bands of many molecules were consistent with the *single mode* Morse oscillator energy expression[30]

$$E_n/hc = (n + 1/2)\omega - (n + 1/2)^2x, \qquad (1)$$

and Figure 1 shows the frequencies of such bands for a variety of molecules, each containing several equivalent X–H bonds. More recently Swofford *et al.*[10] have found that the overtone bands in benzene are unchanged in frequency or width on partial deuteration but decrease in intensity in proportion to the number of remaining C–H bonds; Figure 2 shows the $\Delta v_{CH} = 6$ band as an example. It therefore appears that the X–H bonds oscillate independently (as local modes) in these highly excited levels and that the bands shown have degeneracies equal to the number of equivalent X–H bonds.

Very detailed recent work has fully confirmed this picture and solved a number of

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[18] L. R. Khundar, J. L. Knee, and A. H. Zewail, *J. Chem. Phys.*, 1987, **87**, 77.

[19] N. F. Scherer and A. H. Zewail, *J. Chem. Phys.*, 1987, **87**, 97.

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[23] M. S. Child and L. Halonen, *Adv. Chem. Phys.*, 1984, **57**, 1.

[24] E. L. Sibert, J. T. Hynes, and W. P. Reinhardt, *J. Chem. Phys.*, 1984, **81**, 1115.

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[29] T. Uzer, J. T. Hynes, and W. P. Reinhardt, *J. Chem. Phys.*, 1986, **85**, 5791.

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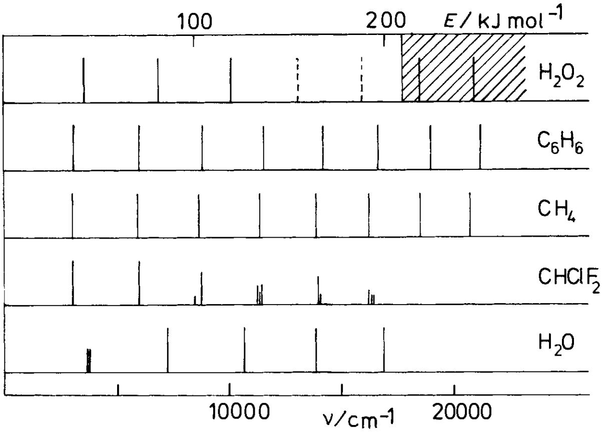

Figure 1 *Frequencies of observed overtone bands. The shaded area lies above the dissociation limit for* H_2O_2

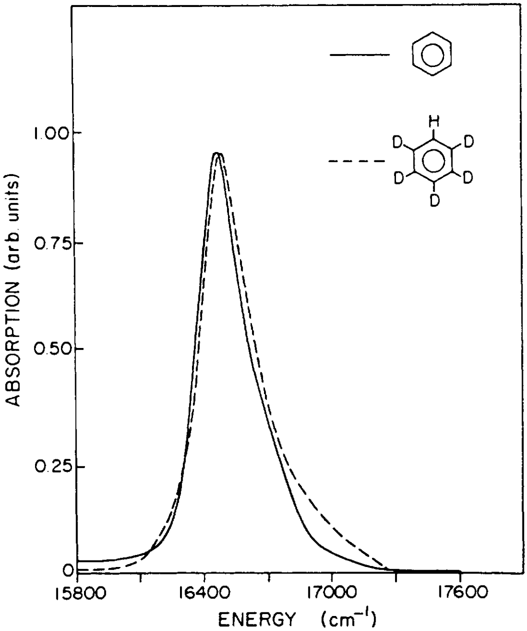

Figure 2 *The* $v_{CH} = 6$ *overtone band of* C_6H_6 *compared with the same band in* C_6D_5H *increased in intensity by a factor of six*
(Reproduced by permission from *J. Chem. Phys.*, 1977, **66**, 5245)

consequent problems, the major difficulty being to account for the simplicity of the spectrum. Even in water, for example, the assignment of five vibrational quanta to two equivalent stretching modes should give rise to six symmetry allowed $\Delta v = 0 \longrightarrow 5$ transitions, of which only a narrowly separated pair ($\Delta v = 0.4$ cm^{-1}) appear at first sight to contribute to the spectrum. On closer inspection, however, three very weak $\Delta v = 5$ OH stretching bands are observed,[31,32] and a fourth band is confidently predicted.[33] Furthermore the relative spacings of these bands, shown in Figure 3, and similar patterns in other molecules, have led to a clear understanding of the factors responsible for the normal mode to local mode transition.

Two competing factors are at work: the interbond coupling responsible for normal coordinate behaviour and the bond anharmonicity, evidenced by the Morse oscillator-like progressions given by equation 1. Classically this competition may be understood by noting that the mutual response of two coupled oscillators varies inversely with the difference between their natural frequencies. Thus the transferability of characteristic C–H stretching frequencies from one molecule to another depends as much on their large frequency separation from other modes as from the absence of coupling.[1] The situation is more subtle in the case of two equivalent bonds because their natural fundamental frequencies must be identical, but in this case the bond anharmonicity causes a frequency decrease as the energy rises. In quantitative terms, the semi-classical identity (equation 2)

$$\bar{\omega} = (E_{n+1/2} - E_{n-1/2})/hc = \omega - (2n + 1)x, \tag{2}$$

between the classical frequency ω and the quantum mechanical level spacing, shows for water (with $\omega = 3\,875$ cm^{-1} and $x = 84$ cm^{-1}) that there is a change of frequency of ~ 840 cm^{-1} between the $v = 5$ and $v = 0$ states, which may be compared with a splitting of only 100 cm^{-1} between the stretching fundamentals, due to interbond coupling. One can therefore see that the interbond coupling will appear relatively strong (near normal-mode-like) in states $|n, m\rangle$ if $n \cong m$, but that the two bonds will oscillate almost independently if their excitation levels are very different ($n = 0$ and $m = 5$ for example). Note that quantum numbers n and m are used to label local excitation states to avoid confusion with the traditional normal model labels v_1, v_2, *etc.*[1]

The quantum mechanical equivalent of the above classical argument is illustrated in Figure 3. The left-hand side shows the energies of the six possible $v = n + m = 5$ two-mode Morse oscillator states together with the dominant $\Delta n = \pm 1$, $\Delta m = \pm 1$ coupling scheme implied by the potential functions used to analyse the spectrum.[34] The right-hand side shows the five observed energies and one predicted level, from which it is apparent that the two directly coupled $|2, 3\rangle$ and $|3, 2\rangle$ levels give rise to a large first order (or normal-mode-like) splitting of 224

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[31] J. W. Swensson, W. S. Benedict, L. Delboiville, and G. Roland, *Mem. Soc. R. Sci. Liege*, special vol. 5, 1970.

[32] L. S. Rothman, *Appl. Opt.*, 1978, **17**, 3517.

[33] M. S. Child, *Chem. Phys. Lett.* 1982, **87**, 217.

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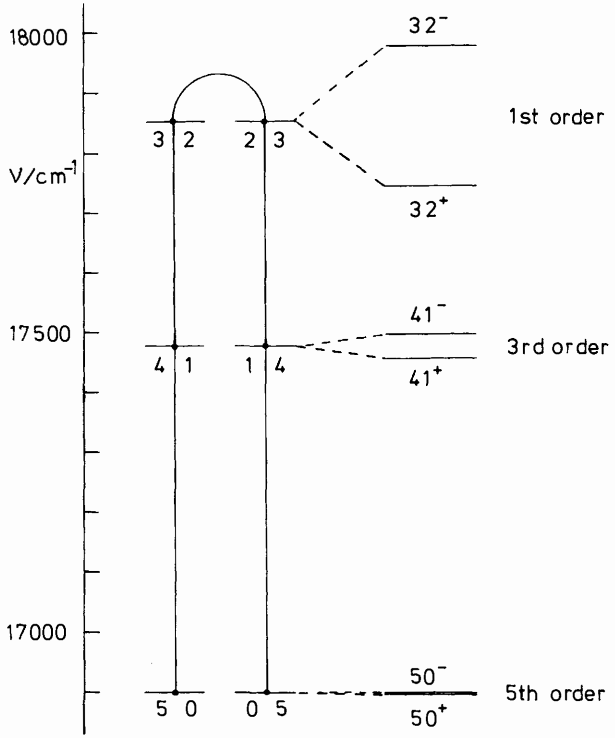

Figure 3 *The local mode coupling scheme and resulting eigenvalue pattern for the $v = 5$ overtone manifold of* H_2O

cm^{-1}, whereas the two lowest levels derived from $|0, 5\rangle$ and $|5, 0\rangle$, which give rise to the predominant absorption bands, are split only in fifth order by 0.4 cm^{-1}.

Furthermore the predominance of the $|5, 0\rangle$ over $|4, 1\rangle$ and $|3, 2\rangle$ bands is readily understood in terms of a localized bond dipole model because the transition intensity from $|0, 0\rangle$ to $|n, m\rangle$ then depends on terms like $\langle 0|\mu|n\rangle\ \langle 0|m\rangle$, and the second factor $\langle 0|m\rangle$ vanishes unless $m = 0$.[22,23]

The overall conclusion is that the strong bond anharmonicity of the X–H stretching modes drastically disturbs the familiar normal mode picture in a way that actually simplifies the appearance of the spectrum. Moreover recognition of this simplicity has led to remarkably accurate predictions of the overtone absorption frequencies of several small molecules.[22] For example the frequencies of the predicted methane bands which are compared with experiment in Table 1 were derived from a model involving only three potential parameters:[35] two to specify the Morse frequency and anharmonicity and one to fix the interbond coupling strength.

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[35] L. Halonen and M. S. Child, *Mol. Phys.*, 1982, **46**, 239.

Table 1 *Observed and calculated* CH *stretching frequencies in methane.*[23] *Assignments of bracketed bands are uncertain.*

v	Γ	$\nu_{obs.}$ (cm^{-1})	$\nu_{calc.}$ (cm^{-1})
1	A_1	2 916.47	2 916.4
	F_2	3 019.49	3 021.0
2	A_1	—	5 791.6
	F_2	5 861	5 856.4
	F_2	6 004.65	6 010.2
3	F_2	8 604	8 612.5
	F_2	8 807	8 807.8
	F_2	8 900	8 909.5
	F_2	9 045.92	9 041.7
4	F_2	11 270	11 262.5
	F_2	(11 620)	11 553.3
	F_2	(11 885)	11 907.2
5	F_2	13 790	13 796.4
	F_2	14 220	14 206.9
	F_2	(14 640)	14 641.1
6	F_2	16 160	16 213.3
	F_2	16 740	16 745.1
7	F_2	18 420	18 513.5
	F_2	19 120	19 166.0
8	F_2	20 600	20 697.4
9	F_2	22 660	22 765.3

3 Fermi Resonance Coupling

The above isolated local mode picture is at best limited to small molecules with high frequency motions and a consequent low density of states. The situation in larger molecules is rapidly complicated by coupling between different types of mode, due in particular to Fermi-resonance types of coupling.[6,23–25] Even the spectra of H_2O and CH_4 are slightly perturbed by Fermi resonance, but the situation becomes much more drastic in benzene, where the CH stretching character is spread over possibly hundreds of molecular eigenstates in any particular overtone band. One therefore thinks of the X–H stretching modes as 'vibrational chromophores'[6] rather than labels for any particular eigenstate.

The transition from H_2O-like to benzene-like behaviour is well illustrated by the low resolution survey spectrum of $CHClF_2$[25] shown in Figure 4. (It should be noticed that the optical path length and absorbing gas pressure have been adjusted to make all bands appear in equal strength, although the intrinsic absorption intensity decreases by orders of magnitude over this frequency range). Three factors are important for the interpretation. First the C–H stretching frequency, $\nu_s \cong 3\,020$ cm^{-1} is roughly twice that of the two C–H bending modes, $\nu_a \cong 1\,350^{-1}$ and $\nu_b \cong 1\,310$ cm^{-1}, while Amrein *et al.*[25] estimate stretch–bend coupling constants of the order of 100 cm^{-1}. Hence a strong Fermi resonance[1] between bands characterized by the composite quantum number (equation 3) may be expected.

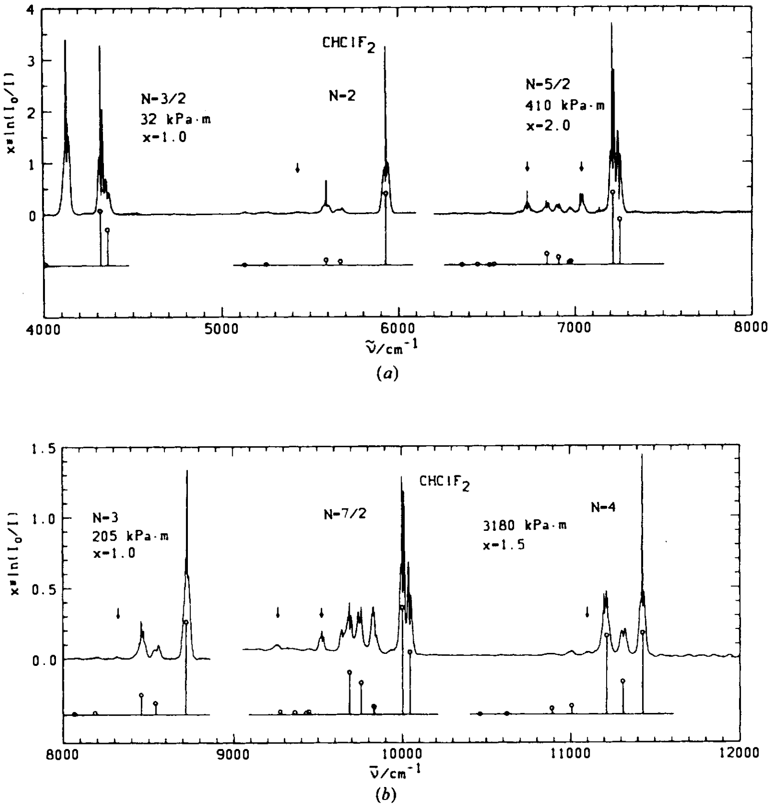

Figure 4 *Survey spectrum of* CHCl$_2$F *in terms of reduced absorbance* $x\ln(I_0/I)$, *with values of* x *and of the product of pressure times path length given in the inserts of the figure. The stick spectra indicate band positions and band strengths calculated from the multiple resonance model.* (Reproduced by permission from *Mol. Phys.*, 1982, **46**, 239)

$$N = v_s + \tfrac{1}{2}v_a + \tfrac{1}{2}v_b \tag{3}$$

Secondly the number of component bands, with given N, increases in proportion to $(N + 1)^2$. Finally the anharmonic constant in equation 1, $x_s \cong 60$ cm^{-1}, of the stretching mode causes the higher v_s level separations to tune towards those of the more harmonic bending modes ($x_a \cong x_b \cong 7$ cm^{-1}), leading to much stronger mixing for $N = 4$ than $N = 2$.

The theoretical model[25] based on these ideas is seen, from Figure 4, to be in remarkably close agreement with the frequencies and intensities of the experimental spectrum. It was assumed that the relative intensities in each so called polyad are all borrowed from the Nth stretching state $|v_s, v_a, v_b\rangle = |N, 0, 0\rangle$, if N is an integer, or from the two dominantly stretching states ($|n, 1, 0\rangle$ and $|n, 0, 1\rangle$) if $N = n + 1/2$.

Thus, for example, the strong band at $N = 2$ corresponds to an almost pure $|2, 0, 0\rangle$ eigenstate while the remaining weaker bands can be assigned to states with $v_s = 1$, $v_b = 2$, or $v_2 = 0, v_a + v_b = 4$. By contrast, at $N = 4$ the mixing is so strong that it is no longer possible to identify the parent $|0, 0, 0\rangle \longrightarrow |4, 0, 0\rangle$ transition; instead there are two roughly equally intense sub-bands plus a third with roughly half the intensity—a picture that persists in the higher frequency $N = 5$ and $N = 6$ visible absorption bands.[36] Although individual peaks can still be identified, the individual quantum numbers v_s, v_a, and v_b have lost their meaning; only the resultant N has a useful physical significance.

This loss of information, or spread of excitation, is taken to a further stage in benzene to the extent that the overtone spectrum[11] consists of a sequence of broad peaks with widths of 30—100 cm^{-1} (see Figures 2 and 5) attributable to successive local mode C–H stretching states coupled to a high density of background states. Sibert *et al.*[24] have followed through the implications of a Fermi resonance model, assuming a geometrically determined interaction between the six CH stretching and six CH wagging modes, with the latter coupled in turn to six C–C stretching modes; furthermore $\nu_{CH} \cong 2\nu_N$ where N includes the two latter types of mode. Figure 5(a) shows that the state density now increases dramatically from one level of the polyad to another, to the extend that the authors[24] could include only the first three levels $|N_{CH}\rangle$, $|(N - 1)_{CH}, 2N\rangle$, and $|(N - 2)_{CH}, 4N\rangle$ in their calculations; but they argue plausibly that inclusion of the complete polyads would merely fill in the gaps in Figure 5(b) to give smooth looking peaks with widths in excellent agreement with those found experimentally.[11] Each line in Figure 5(b) should also be broadened by rotational structure for comparison with experiment, although this 'heterogeneous' contribution (due to a superposition of distinct vibrational spectra from different initial rotational states) to the band width is likely to be quite small in benzene in view of its very small rotational constants.

The conclusion from this calculation is that benzene has no simple high excited C–H overtone states. Instead the CH excitation is at least spread over a forest of CH wagging and C–C stretching states, coupled to it by Fermi resonance. The extent to which this coupling extends to other vibrational degrees of freedom (of which there are 30 in benzene, all told) remains, however, to be established.

4 Intramolecular Vibrational Relaxation

The above picture of almost complete quantum mechanical mixing can also be cast in the time domain in terms of intramolecular vibrational relaxation at a rate determined by the width of the band. Imagine the (no longer quite hypothetical[18,19]) 'instantaneous' excitation of a pure local mode state Φ_0 which by our previous assumptions carries the entire oscillator strength of the band. Since Φ_0 is not a stationary state (*i.e.* not a strict eigenstate), its composition will change with time. The probability of remaining in the original state for time t may, however, be calculated as $|\langle\Phi_0(0)|\Phi_0(t)\rangle|^2$, which is shown below to decrease at a rate proportional to the width of the band.

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[36] J. S. Wong, Dissertation, Berkeley, 1981.

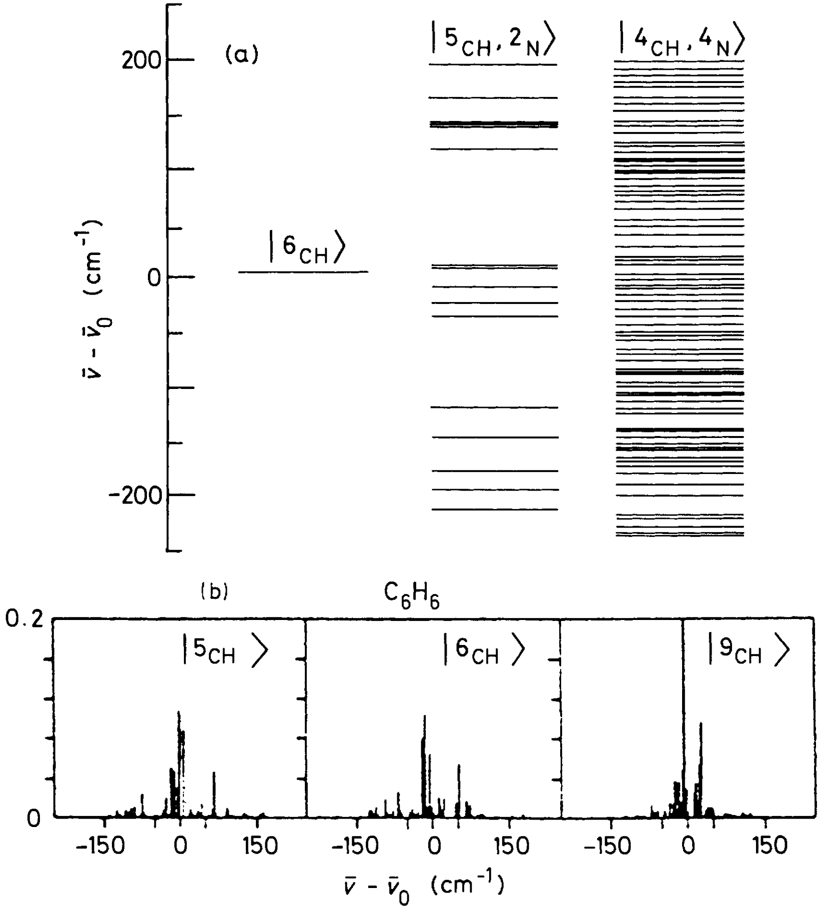

Figure 5 *A diagram to show (a) the increasing density of Fermi coupled levels responsible for the* $|6_{CH}\rangle$ *band of benzene, and (b) the resulting calculated structure for the* $|5_{CH}\rangle$, $|6_{CH}$, *and* $|9_{CH}\rangle$ bands
(Reproduced by permission from *J. Chem. Phys.*, 1984, **81**, 1115)

The mathematical argument is as follows. Let φ_i denote a set of zeroth order time-independent wavefunctions, labelled by recognizable quantum numbers, and let φ_0 be the pure X–H overtone state. A typical eigenstate ψ_n may then be represented (equation 4) as

$$\psi_n = \sum_i c_{ni}\varphi_i \tag{4}$$

where c_{n0}, which determines the absorption strength, will be assumed consistent with a Lorrentzian profile

$$|c_{n0}|^2 = (b/\pi)/[(\omega_n - \omega_0)^2 + b^2] \tag{5}$$

normalized such that

$$\sum_n |c_{n0}|^2 \cong \int_{-\infty}^{\infty} |c_{n0}|^2 d\omega_n = 1 \tag{6}$$

where $\hbar\omega_n$ denotes the energy of ψ_n. Now equation 4 may be inverted to give, in particular,

$$\varphi_0 = \sum_n d_{0n}\Psi_n \tag{7}$$

and the orthogonal nature of the transformation[7] ensures that $d_{0n} = c_{n0}$. Equation 7 applies, however, only at time $t = 0$. It is replaced at later times by[37]

$$\Phi_0(t) = \sum_n c_{n0}\Psi_n e^{-i\omega_n t} \tag{8}$$

The survival probability in state Φ_0 is therefore determined

$$\begin{aligned}\langle\Phi_0(0)|\Phi_0(t)\rangle &= \sum_{n,n'} c^*_{n'0}c_{n0}\langle\psi_{n'}|\psi_n\rangle e^{-i\omega_n t}\\ &= \sum_n |c_{n0}|^2 e^{-i\omega_n t}\\ &\cong \frac{b}{\pi}e^{-i\omega_0 t}\int_{-\infty}^{\infty}\frac{e^{-i(\omega_n-\omega_0)t}}{[(\omega_n-\omega_0)^2+b^2]}d\omega_n\\ &= \frac{b}{\pi}e^{-i\omega_0 t}\int_{-\infty}^{\infty}\frac{\cos(\omega_n-\omega_0)_t}{(\omega_n-\omega_0)^2+b^2}d\omega_n\\ &= e^{-i\omega_0 t - bt}\end{aligned} \tag{9}$$

Here the orthogonality relation $\langle\psi_{n'}|\psi_n\rangle = \delta_{nn'}$ has been used in the first line, and the following standard integral[38] has been employed

$$\int_0^{\infty}\frac{\cos\alpha x}{x^2+\beta^2}dx = \left(\frac{\pi}{2\beta}\right)e^{-\alpha\beta} \tag{10}$$

The final result, as promised, is equation 11

$$|\langle\Phi_0(0)\Phi_0(t)\rangle|^2 = e^{-2bt}, \tag{11}$$

where the time constant, $2b$, of the exponential decay is readily seen to correspond with the full width at half maximum of the assumed spectroscopic profile in equation 5.

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[37] P. W. Atkins. 'Molecular Quantum Mechanics'. 2nd Edn., Oxford University Press.

[38] H. B. Dwight, 'Tables of Integrals'. 4th Edn., Macmillan. 1961.

Notice that this derivation says nothing about the density of lines in the profile. All that is required is that the number with perceptible intensity should exceed say 10, in order to justify replacement of the sums in equations 6 and 9 by integrals. The line density is, however, extremely interesting in this general context because it relates directly to the number of degrees of freedom into which the initially excited state $\Phi_0(0)$ relaxes.

These considerations explain the current interest in two exciting areas of spectroscopy. On one hand there is a drive to develop femto-second laser techniques[18,19] in order coherently to excite full band profiles in a time that is short compared with their relaxation time. Secondly, one seeks frequency-locked continuous wave lasers with the resolution to detect single eigenstates in situations where the line density may reach 100 lines per cm^{-1}. Both types of experiment have been brought to bear on the problem of intersystem crossing in pyrazine,[39,40] which is conceptually very similar to that of overtone relaxation, but without the added technical problem of very low oscillator strengths.

5 Overtone Induced Dissociation

It is evident from Figure 1 that excitation to the $v_{\text{OH}} = 6$ overtone level of hydrogen peroxide provides sufficient energy to break the O–O bond. Recent experimental[26,27] and theoretical[28,29] studies of this process raise a number of interesting questions.

The first point is that the crude width ($\approx 86\ \text{cm}^{-1}$ of the room temperature overtone band, shown in the right hand upper panel of Figure 6, would imply a dissociation lifetime, $\tau \cong 0.05$ ps, which is seriously at variance with RRKM-like estimates[28] of 5—50 ps and with a detailed dynamical estimate[29] of about 8 ps. The middle panels of Figure 6 show however that the apparent band width can be seriously misleading with respect to the dissociation lifetime for a molecule with as large a rotational constant as H_2O_2. ($A \cong 10\ \text{cm}^{-1}$ for rotation about the O–O axis) because inhomogeneous rotational broadening, estimated[29] as $2(2AkT)^{\frac{1}{2}} \cong 80\ \text{cm}^{-1}$, can account for the entire profile. It is, in any case, apparent from the upper panels of Figure 6 that the $4\nu_{\text{OH}}$ band which cannot excite dissociation has much the same width as the $6\nu_{\text{OH}}$. The lower panels show, however, that jet cooled samples,[27] with only the few very lowest rotational states populated, give quite different pictures for the $4\nu_{\text{OH}}$ and $6\nu_{\text{OH}}$ bands. The former is ultimately resolvable into individual lines with widths of the order $\Delta\nu \cong 0.08\ \text{cm}^{-1}$, which are governed by experimental factors. The $6\nu_{\text{OH}}$ band is also drastically simplified by jet cooling but the features are substantially broader, and the authors[27] conclude, after careful tests, that this breadth is due predominantly to homogeneous lifetime broadening. They take the $1.5 \pm 0.3\ \text{cm}^{-1}$ of the narrowest feature near $18\,942\ \text{cm}^{-1}$ as setting a lower limit on the dissociation lifetime ($\sim 2\pi c\Delta\nu$) of 3.5 ps, in good agreement with the above theoretical estimates.[28,29]

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[39] B. J. van der Meer, H. T. Jonkman, J. Kolmmandeur, W. L. Meerts, and N. A. Majewski, *Chem. Phys. Lett.*, 1982, **92**, 565.

[40] B. J. van der Meer, H. T. Jonkman, G. ter Horst, and J. Kommandeur, *J. Chem. Phys.*, 1982, **76**, 2099.

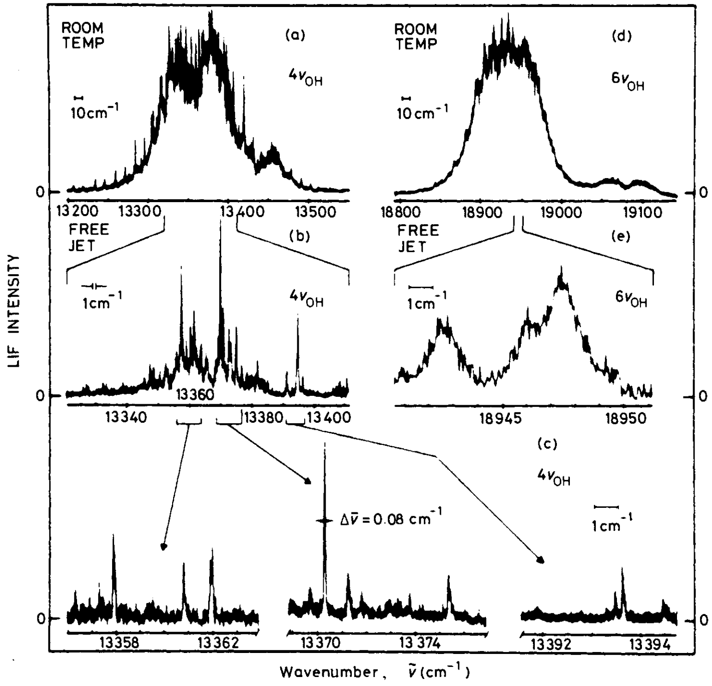

Figure 6 *Spectra of vibrational overtone transition to a bound state* ($4\nu_{OH}$) *and to a predissociative state* ($6\nu_{OH}$) *of hydrogen peroxide; (a) and (d) were taken at low resolution from room temperature samples; (b), (c), and (e) are high resolution spectra from jet-cooled samples. Note the marked difference in line width between (c) and (e), indicative of homogeneous like-time broadening in the* $6\nu_{OH}$ *band*
(Reproduced by permission from *J. Chem. Phys.*, 1986, **85**, 2331)

The two calculations give, however, rather different pictures of the dissociation dynamics. Dubäl and Crim[28] use an RRKM-like statistical adiabatic channel model[41] based on the assumption that the energy from the initial OH stretching motion is equilibrated between all internal degrees of freedom before dissociation. Uzer *et al.*,[29] on the other hand, follow the classical dynamics on a spectroscopically based potential energy surface, and find that the energy flow is by no means completely statistical. A fairly close (but not exact) Fermi resonance leads to rapid (0.2 ps) partial energy exchange between the initially excited oscillator and the directly coupled H–O–O bend. There is also some excitation transfer to the second O–O–H bending motion, but no smooth energy build-up in the O–O dissociation mode, nor any significant energy transfer to the second OH stretch or to the two torsional degrees of freedom. Instead the O–O bond appears to break

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[41] J. Troe, *J. Chem. Phys.*, 1983, **79**, 6017.

when the system reaches some as yet uncharacterized (Slater-like?) critical configuration.

Information about the internal states of the nascent OH fragments also bears on the question of statistical or non-statistical energy flow, because the energy of the $v_{OH} = 6$ stretching state exceeds the dissociation energy by roughly 20 kJ (1 600 cm^{-1}), which is sufficient to populate at least the $J = 8$ rotational state of OH, and populations up to $J = 10$ are reasonably accessible from a room temperature sample. Rizzo *et al.*[26] find, by laser-induced fluorescence, that the OH and OD fragment rotational population, from the $6v_{OH}$ overtone dissociation of HOOH and HOOD are consistent with a statistical distribution over product states which is in turn consistent with (but not strictly dependent on) a statistical energy distribution over the molecular modes before dissociation. On the other hand a weak band at the slightly higher frequency $6v_{OH} + 385$ cm^{-1}, gives rise to a shift in the fragment rotational distribution to lower J values, contrary to the prediction of any statistical model.[26] As a further test it would be very interesting to see whether the product rotational distributions from jet cooled samples are similar to those obtained at room temperature in case the 'statistical' product state distribution arises from statistical averaging over initial populations rather than from statistical dynamics during the dissociation process. Another interesting experiment would be to examine the relative OH($v = 1$) and OD($v = 1$) product yields from higher nv_{OH} overtone bands of HOOD, because extrapolation of the dynamical results[29] would predict only vibrationally excited OH. Unfortunately, however, the interpretation would be complicated by the possible influence of a second electronic state at energies above the $v_{OH} = 7$ energy level.

Further information on the extent to which an initial OH excitation is distributed over the molecule is in principle contained in the line densities of the $4v_{OH}$ band. (Similar information from the $6v_{OH}$ band would be even more interesting, but the homogenous line broadening due to dissociation will probably prohibit the necessary resolution.) Butler *et al.*[27] estimate a mean density of 3.6 vibrational lines per cm^{-1} at the $4v_{OH}$ energy level if the OH excitation were shared between all degrees of freedom, whereas the density of moderately strong lines in Figure 6(c) is at best one per cm^{-1} and some at least of these come from initially rotationally excited levels. Hence there is again an indication that the energy flow is not fully statistical.

6 Conclusions

Several conclusions can be drawn from these new spectroscopic experiments. In the first place we are reminded that the normal coordinate picture of vibrational modes is dependent on the harmonic approximation, and it has been shown that the anharmonicity of X–H stretching potentials leads to a transition from the normal mode to a local mode picture. Moreover the relatively high intensity of X–H overtone transitions provides a series of windows for investigation into the nature of intramolecular dynamics.

In considering the extent of intramolecular relaxation from X–H stretching modes to other degrees of freedom, Fermi resonance coupling to neighbouring

X–H bending modes was seen to provide probably the fastest general relaxation mechanism. Alternatively, in the frequency domain, Fermi resonance provides the dominant contribution to the breadth of the band over which the X–H overtone state is spread. Conversely the density of lines within the band in principle gives a measure of the number of significantly coupled degrees of freedom, but the measurement of such densities puts a high premium on the spectroscopic resolution.

Finally the overtone induced dissociation of hydrogen peroxide was shown to offer direct insight into the detailed mechanism of the decomposition process. Careful line width measurements fix the rate; laser-induced flourescence can assess the statistical or non-statistical nature of the energy disposal over fragment states; and the line density of neighbouring non-dissociative bands can give information about the number of coupled degrees of freedom. At present there is information both for and against a purely statistical picture of the dissociation. The weight of evidence favours a less than fully statistical description, but it will be interesting to see how the balance tilts in the light of future experiments.

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