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# SPECTRA AND DYNAMICS OF COUPLED VIBRATIONS IN POLYATOMIC MOLECULES

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# INTRODUCTION

The spectra and dynamics of coupled vibrational states in polyatomic molecules have for a long time been a central theme of physical chemical research (1-3). Recently, a major change in emphasis and an explosive development of the subject has occurred, because of great changes in several related areas:

- 1. During the last two decades Fourier transform and laser spectroscopy techniques have made high resolution infrared spectra close to the Doppler limit with the possibility of detailed rovibrational analysis much more easily accessible than before (4–7).
- 2. The development of special techniques with greatly increased sensitivity has permitted the measurement of the weak spectra associated with high overtones of vibrations in the near infrared and visible (8–12).
- 3. The spectroscopy of molecules cooled to very low internal temperatures in supersonic free jet expansions has been used to obtain analyses of spectra for molecules and complexes, whose spectra at room temperature are much too complicated for analysis (13–17).
- 4. The understanding of the complex spectra of coupled vibrations has become important for newly developing fields of molecular reaction dynamics such as infrared laser chemistry (18–22) or vibrational overtone photodissociation (23–26).

- 5. The relation of the dynamics of coupled vibrations with the "classical" problems in unimolecular reaction rate theory has emerged in a new light (27–31).
- The new understanding of classical dynamical systems showing deterministic chaos has raised important, largely unsolved, fundamental questions relating to the dynamics of coupled molecular vibrations (32–39).
- 7. Ab initio quantum calculations are now possible, which provide a realistic picture of the spectra of polyatomic molecules (40–51).

The present review summarizes some selected topics in this vast field of research. The basic questions the reader should have in mind are: How does a specific, local, or global vibrational excitation in a highly excited polyatomic molecule evolve in time? How is this dynamical process reflected in the stationary, time-independent high resolution spectra of molecules? How can we obtain and analyze such spectra in order to resolve the foregoing questions? Which theoretical concepts for the understanding of the vibrational dynamics have emerged as a result of current investigations?

In addition to the reviews and examples mentioned above there have been a few special issues of journals, books, and reviews, which may serve as a complement to this article (52–66). This review is by no means meant to be exhaustive, but is intended to highlight certain developments, particularly well known to the author, to extend and complement existing views and surveys rather than to duplicate them. It is thus quite in the spirit of this series of reviews. Apologies are extended to those authors, whose work is less than adequately referred to.

We first outline some of the current experimental techniques. Then we discuss anharmonic resonances such as coupling of stretching and bending motions with emphasis on the CH chromophore in polyatomic molecules. Quite a different kind of coupling exists between "local mode" stretching excitation of similar bonds (the two OH in  $H_2O$ , the NH in NH<sub>3</sub>, CH in CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> etc), and we present in one chapter the currently popular field of "local modes" briefly, but from a slightly different (also historical) perspective than usual. We also discuss some aspects of "statistical spectra" and coupled vibrational states of molecular complexes and clusters, as well as the relation to current ab initio calculations of molecular spectra.

# NEW EXPERIMENTAL TECHNIQUES FOR THE HIGH RESOLUTION SPECTROSCOPY OF COUPLED MOLECULAR VIBRATIONS

Compared to the traditional methods of spectroscopy, which provided the basis of the empirical knowledge about molecular vibrations until about

1970 (1, 2), some significant advances have been made in several directions. Fourier transform and laser absorption spectroscopy have provided much higher resolution, now often close to the Doppler limit even in the IR (typical resolutions from 10 to 100 MHz can be attained almost "routinely" in many advanced experiments). Special detection techniques such as photoacoustic laser spectroscopy or intracavity laser techniques or simply very long absorption paths using multiple reflection optics have increased sensitivity for weak absorptions, particularly important for high overtones. Various double (or triple) resonance schemes have also helped to increase both sensitivity and state selectivity. Perhaps the most important general approach, which can be used with many of the methods mentioned and is central in helping to unravel the information contained in the normally much too complex spectra, is the cooling of molecules in supersonic jet expansions, while retaining vapor-phaselike isolation or even selectively generating small clusters by very limited condensation.

This chapter reviews some of the most significant advances towards techniques of general applicability in recent years. More specialized techniques are mentioned only briefly and incompletely.

# Supersonic Jet FTIR and Laser Spectroscopy

Cooling the internal degrees of freedom in supersonic free jet expansions has been one of the major aids in the analysis of molecular rovibrational spectra. The earliest experiments used highly sensitive detection techniques such as molecular beam electric resonance (67) or laser induced fluorescence (68, 69). The early work has been reviewed (70), and most of this and subsequent work deals with UV-VIS fluorescence spectroscopy, which are not discussed here. Advances in rovibrational spectroscopy were first restricted to laser techniques (13-15, 65, 71-79). Ordinary IR absorption spectroscopy was carried out with grating spectrometers at very modest resolution (80a,b) and with FTIR spectroscopy at resolutions of up to  $0.06 \text{ cm}^{-1}$  (16). Resolution is an important consideration, because in order to optimize the signal in line spectra and simplify analysis, the instrumental bandwidth should be of the order of the Doppler width as obtained when viewing the free jet perpendicular to the direction of expansion. Such a resolution is also necessary in order to obtain accurate (relative and absolute) line intensities from such spectra, because there are serious distortions if the instrumental bandwidth is larger than the Doppler widths.

We have developed in Zürich FTIR-supersonic jet spectroscopy (17, 81-90) under conditions that often satisfy the requirement of Doppler limited resolutions (instrumental bandwidth 0.0024 cm<sup>-1</sup> or 72 MHz, unapodized). The current spectrometer system is shown schematically in



*Figure 1* Scheme of the supersonic jet FTIR spetrometer system built in the Zürich group (17, 90). The BOMEM DA.002 interferometer optics (optical retardation 2.50 m) is drawn in a simplified manner (the moving mirror  $M_2$  really moves perpendicular to this top-view plane). The rest is drawn as a close to real top view. The vacuum systems of the interferometer and the nozzle (N) chamber are totally separated by windows W. Conventional symbols are used for the components. Optical components and detectors (D) cover the range 10 to 16,000 cm<sup>-1</sup> (see also descriptions in Refs. 17, 90).

Figure 1. It integrates the continuous supersonic jet expansion in the sample compartment, but is separated from the vacuum system of the interferometer by windows (W in Figure 1). The first system used an external jet cavity (81). Figure 2 shows as an example the IR spectrum of CO, demonstrating the rotational cooling as a function of distance from the nozzle and the Doppler broadening. The effective Doppler width increases as a function of distance from the nozzle from 0.0055 cm<sup>-1</sup> to 0.0069 cm<sup>-1</sup> (effective "temperatures" of 360 to 515 K). Thus without skimming of the beam, there is no reduction of the Doppler width. However, rotational temperatures decrease from room temperature to 13 K 2 mm after the nozzle and to 6 K at about 11.5 mm after the nozzle. In essence, energy in the internal degrees of freedom is transformed into translational energy in the direction of the expansion, following the equation for enthalpy  $H_i$  (before) and  $H_f$  (after the expansion)

$$H_{\rm i} = H_{\rm f} + \frac{1}{2} {\rm mv}^2$$



Figure 2 FTIR-jet Spectrum of CO, taken at a distance of z' = 11.5 mm (=z+0.5 mm). Upper part: simulation with  $T_{\text{rot}} = 6 \text{ K}$ ; lower part: experiment, showing a small high temperature background from the vacuum chamber. As a function of distance z' from the nozzle one finds the following results for Doppler widths  $\Delta \tilde{v}_D$  (corrected for instrumental width), Doppler velocity perpendicular to the beam,  $v_D$ , and rotational temperature,  $T_{\text{rot}}$ :

<i>z'</i> /mm	$\Delta \tilde{v}_{\rm D}/{\rm cm}^{-1}$	$v_D/ms^{-1}$	$T_{ m rot}/{ m K}$
2	0.0055	385	13.2
3	0.0057	400	10.0
4	0.0061	425	8.6
5.5	0.0067	470	7.2
7.5	0.0069	480	6.5
11.5	0.0069	480	5.9

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Of course  $H_f = 0$  cannot be attained because the collision rate goes to zero upon expansion into the vacuum. The rotational temperatures can often be well represented by the approximate equation (91, 92)

$$T = T_{\infty} + T_0 [1 + \frac{1}{2}(\gamma - 1)M^2]^{-1}$$
ith the Mach numbers  $M, M_0$ 

$$M = M_0 - \frac{1}{2}(\gamma + 1)[(\gamma - 1)M_0]^{-1}$$
3.

W

$$M_0 = A[(Z - Z_0)D^{-1}]^{\gamma - 1}.$$
4.

For CO, the ratio of specific heats is  $\gamma = C_p/C_v = 7/5$ . *D* is the diameter of the nozzle (0.1 mm in the example). For *A* one may take an empirical value (92) of 3.65 and  $Z_0 \simeq 0.4D$  (*T* and *M* without index are taken as a function of distance *Z*). Of course, similar spectroscopic results can be obtained by laser spectroscopy, if lasers are available. However, the great advantage of FTIR spectroscopy is the large spectral range covered by a single experiment (typically 300 cm<sup>-1</sup> at full resolution, the constraint arising from optical filtering) and even more so in separate experiments. So far we have used the technique from about 800 cm<sup>-1</sup> [on CHClF<sub>2</sub> (89)] to around 3400 cm<sup>-1</sup> [propyne, ethyne, etc (17)]. In principle, our system covers the range from about 10 cm<sup>-1</sup> to 16,000 cm<sup>-1</sup>.

Figure 3 illustrates in a survey spectrum with the example of the Coriolis coupled pair  $v_3$ ,  $v_8$  of CHClF<sub>2</sub> (84), how two completely merged bands separate in the supersonic jet spectrum, which has given a starting point for the analysis of the spectrum at room temperature and the determination of the Coriolis coupling (93). Another example is provided by the highly congested spectrum of  $v_1/2v_5$  in CF<sub>3</sub>Br, which becomes strikingly simple at low temperatures in the jet (85) (Figure 4). So far, useful results have been obtained for the electronic relaxation of NO (17), CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>CCH,



*Figure 3* Spectrum of the Coriolis coupled pair  $v_3$  (1108.7292 cm<sup>-1</sup>) and  $v_8$  (1127.7854 cm<sup>-1</sup>) in CH<sup>35</sup>ClF<sub>2</sub> (in natural abundance). At room temperature (rt) the spectra overlap completely in the intermediate range between the centers (left- and right-hand ends of figure). In the jet (simulation, sim, at  $T_{rot} = 50$  K), the bands are well separated (84). Coriolis constant  $\zeta_{3,8}^a = 0.56$  cm<sup>-1</sup> (94). [Reproduced by permission from *Chem. Phys. Lett.* (84).]



*Figure 4* Spectrum of the Q-branch region of the  $v_1$  fundamental in CF<sub>3</sub><sup>79,81</sup>Br (natural mixture). At room temperature the spectrum is highly congested. At low rotational temperature ( $T_{rot} = 45$  K) in the jet the Q-branches of the two isotopomers are easily recognized. The hot band  $v_1 + v_6 - v_6$  (1083.52920 and 1083.28457 cm<sup>-1</sup>) indicates a vibrational temperature  $T_{v_6} = 230$  K. [Reproduced by permission from *Infrared Physics* (85).]

CHF<sub>3</sub> (CH stretching bands; 17), N<sub>2</sub>O, CBrF<sub>3</sub> (85; CF<sub>3</sub> stretching range), CF<sub>3</sub> I (85, 88), CHClF<sub>2</sub> (84, 89, 93; several bands from 800 to 3100 cm<sup>-1</sup>), CHCl<sub>2</sub>F, and CFCl<sub>3</sub> (87). Recently, jet FTIR spectroscopy at medium resolution has been used for the study of clusters (94). Benzene and pyridine have been studied (95). The most serious limitation of the technique is the limited sensitivity. One can improve the sensitivity by using conventional techniques such as multipass optics similar to laser spectroscopy systems (96; M. Nota, M. Quack, U. Schmitt, and M. Snels, unpublished). One could also try to use an optical nulling technique to measure the very weak absorptions (98). However, in principle, one could go much further (M. Quack, unpublished): The detector for optical transmission could be supplemented by an ion extraction-mass spectrometer system and the crossing point of molecular beam and interferometer beam excited by pulsed visible (UV) lasers to obtain a multiphoton ionization signal from the molecules that are irradiated with the IR light. Because of the simultaneous IR excitation, the multiphoton ionization signal depends on the position of the moving mirror  $M_2$  (in Figure 1) and thus provides an "interferogram" when measured with a time resolved facility (97). If such a system could be realized, technically (with pulsed jets), it obviously would solve the problem of sensitivity, although the detection technique is not generally applicable to all molecules (depending on the threshold for multiphoton ionization and its sensitivity to IR excitation). With mass spectrometric detection, one might, however, have additional selectivity to certain substances in mixed jets and thus at the same time obtain an analytical tool. There have been other advances, such as FT-Raman spectroscopy (99), polarization modulation (100), or simply new instruments (101) that could be used in conjunction with the supersonic jet technique.

Less speculative is clearly the increased sensitivity provided by IR-laser spectroscopy of supersonic jets. This can be obtained by gated (phase sensitive), direct absorption techniques (15, 102–116) or by bolometric detection (13, 76, 117–121) and intracavity laser techniques (122; F. Stoeckel, private communication 1989).

The current bolometric detection laser experiments typically use difference frequency laser systems (123, 124) or F-center lasers (125–128), and thus the frequency range is still limited to the near infrared, where the high frequency fundamentals occur. This is not a limitation of principle but is related to the availability of strong lasers. One should particularly note the work, using this technique, on overtones of high frequency vibrations (76, 118, 119). Among the more specialized techniques is the study of free radicals (NH<sub>2</sub>) in jets (131). "Sliced jets" produce narrow Doppler holes in the line profile, allowing for a sort of sub-Doppler spectroscopy (129), and another hole burning technique to probe inhomogeneous structure has been demonstrated as well (130).

# Photoacoustic Laser Spectroscopy

Direct absorption spectroscopy of gases has inherent limitations of sensitivity for weak absorptions. For example, with FTIR techniques, optical path lengths in multireflection cells are currently limited to between 20 and 500 m, typically (132, 136). With laser spectroscopy one can go slightly beyond these values (in direct, simple absorption experiments). In practice then, the highest overtones that can be observed correspond to 5 quanta of CH stretching vibrations, which results in absorption in the red part of the visible spectrum (700 nm for alkyl CH, for example). These spectra are then also pressure broadened. If one wants to go to higher excitation, small pressures, or high dilutions (in analytical work), photoacoustic detection is ideal. The small amount of absorbed energy is dissipated as heat in a gas, resulting in periodic pressure variations that are detected as "sound," for instance by a microphone (133). The method has found substantial use in vibrational overtone spectroscopy and has had a profound influence on our knowledge of high excited vibrational states (8–11, 134–139). The photoacoustic technique is now well proven, but further significant experimental advances have been made. An example is the recent work of Davidsson et al (140), in which the sensitivity of the technique has been greatly improved.

# Intracavity Laser Absorption Spectroscopy (ICLAS)

A most interesting technique to obtain extremely long effective absorption paths is to place the absorbing species inside the active cavity of a broadband laser, for instance a dye laser in the visible (141–145) or a color center laser in the infrared (146). In practice, a laser operating for some generation time  $t_g$  with an intracavity absorber [molecular absorption cross section  $\sigma(\tilde{v})$ ] emits a spectrum of a typical bandwidth of 100 cm<sup>-1</sup> (FWHM), say around 14,000 cm<sup>-1</sup> (700 nm). The spectrum of intensity *I* is approximately Gaussian, centered at  $\tilde{v}_0$ , but modified by the absorber according to the following fundamental equation (141–143)

$$I(\tilde{v}, t_g) = I_0(\Gamma t_g/\pi)^{1/2} \exp\left[-\left(\frac{\tilde{v} - \tilde{v}_0}{\Delta \tilde{v}_0}\right)^2 \Gamma t_g\right] \exp\left[-\sigma(\tilde{v})Cl_{eq}\right]$$
 5.

 $\Gamma$  is the damping rate of the laser cavity, and the last factor in the equation is the Lambert Beer law with the particle density C and an equivalent optical path length

$$l_{\rm eq} = c \cdot t_{\rm g} \cdot (l/L) \tag{6}$$

where c is the speed of light and l/L is the ratio of the lengths of the absorption cell and the laser cavity. This provides effective path lengths of the order of 10 km, with generation times  $t_g \simeq 50 \ \mu s$ . This most interesting technique has the advantage of directly providing absolute absorption cross sections and has been used particularly by the Grenoble group to study high overtones of polyatomic molecules (143–148).

# Stimulated Emission Pumping (SEP) and Other Double Resonance Techniques

Instead of increasing sensitivity or effective optical path length to study the weak vibrational overtone transitions in the near infrared and visible region, one can also use methods unrelated to direct absorption and thus "break the infrared dipole selection rules." This can be done passively, as in the classical techniques of Raman spectroscopy (149, 150) and molecular resonance fluorescence spectroscopy (151–156) from excited electronic states to the ground state. Resonance Raman spectroscopy can be considered to range intermediate between the ordinary Raman effect and resonance fluorescence. If instead of passively observing fluorescence one "stimulates" it, say with a tunable laser, one has the very powerful technique of "stimulated emission pumping" (157–159). This has been recently reviewed (160). Since then, there have been a few special developments and applications, such as combination with single vibronic level fluorescence (155), the study of transients (CH<sub>2</sub>, 161) and other special topics (162–164).

A number of other double resonance techniques have also found use in the study of vibrationally excited states; for example, microwave detected, microwave-optical double resonance, applied to  $NH_3$  (165). Other approaches to microwave optical double resonance have been discussed (166). Furthermore, IR-IR double resonance has found use (167, 168). Two different types of IR-UV double resonance have been used to probe vibrational states. A molecular beam technique was presented by Lee's group at Berkeley for the study of benzene (169). A most interesting technique has also recently been presented by M. Lester and coworkers (170), who generate complexes of OH with Ar and probe the spectroscopy of overtones of the OH-stretching vibration in Ar OH by near IR-excitation followed by UV laser excitation and fluorescence detection.

# Vibrational Predissociation Spectroscopy (VPS)

In ordinary spectroscopy one observes the interaction of light with molecules (in absorption, emission or otherwise). One may also look with a sensitive technique at either photodissociation products or reactant depletion after monochromatic, tunable vibrational excitation: One then has "vibrational predissociation spectroscopy," a term coined in (171) for the experiments of Crim and coworkers (23–25, 172, 173). The method can be used both for measuring product state distributions and thus probing dissociation dynamics and for measuring the spectrum of the absorbing molecule above the dissociation threshold. A typical scheme is shown in (173). The spectrum measured by means of the product signal will be proportional to the absorption spectrum if the quantum yield is constant and if the probability of forming a certain product state, which is being probed, is constant. Otherwise the relation between signal and absorption spectrum is more complicated. The spectrum of stable vibrational states can be measured by means of vibrationally mediated photodissociation (174).

The depletion of reactant in a molecular beam appears as loss of bolometer signal in the VPS of molecular complexes and clusters by infrared radiation (119, 175–177). There have been numerous applications of this type, but also some recent developments in NIR-VIS VPS of ordinary molecules (178). The group at Troitzk has used VPS to study spectra of highly excited molecules after IR-multiphoton excitation, and this work has recently been reviewed quite extensively (64).

# Special Techniques for the Study of Vibrational States

There are quite a few further special techniques that provide relevant information about coupled vibrational states. Grating spectrometers provide high quality, high resolution spectra in the photographic infrared (179–181). Doppler tuning of accelerated ions of well-defined energy through resonance with fixed frequency provides unprecedented resolution, also as a form of VPS (182). Stark tuning spectroscopy involving excited electronic states and predissociation (183) as well as the eigenstate analysis of coupled electronic states by means of ultrahigh fluorescence excitation and quantum beat spectroscopy (184, 185) provide vibrational state information in some cases. Thermal lensing laser spectroscopy of liquids is used on high overtones (186). Fluorescence polarization spectroscopy of polyatomic molecules has been used for the study of rotation vibration interactions (187). Laser magnetic resonance and related techniques can be used on paramagnetic species. This and related fixed frequency laser techniques provide often extremely high resolution in small ranges, but at the expense of a broad survey, which is also often necessary for a good *understanding* of the spectral structures. We do not attempt completeness here for the many special techniques but turn now to this question of understanding.

# UNDERSTANDING ANHARMONIC INTERACTIONS AND RESONANCES BETWEEN COUPLED VIBRATIONS

The experimental advances reviewed in the preceding section have been essential in helping to assign properly and analyze the observed spectral structures, and also have greatly extended the range of accessible, often highly excited, vibrational states. With respect to our understanding of coupled vibrations, our aims are mainly:

- 1. formulation of appropriate (perhaps simplified) molecular Hamiltonians for the anharmonically coupled vibrations;
- 2. comparison with anharmonic theoretical potentials, for example from quantum chemical ab initio calculations of anharmonic force fields or, perhaps, systematic empirical generalizations of potential models;
- 3. proper analysis of the relevant intramolecular dynamics both in terms of stationary states and time dependent evolution.

The goal of this chapter is then to summarize recent advances in the area with emphasis on one specific example in which a notable progress has been made: *the isolated CH chromophore* (193) in polyatomic organic molecules. This chromophore is associated with complex spectral structures from the infrared to the visible and provides a window for looking at anharmonic interactions between molecular vibrations. Before addressing specific questions, let us contemplate here two general, quite different, types of crowded spectral structures that arise from anharmonic interactions of a chromophore vibration with the remainder of the molecular vibrations:

- 1. *Homogeneous structure* arises if one initial state can be coupled with substantial line strength to several close lying final states.
- 2. Inhomogeneous structure arises if several initially populated states (for instance, in a thermal Boltzmann distribution) give rise to absorption at slightly different frequencies.

Both of these spectral structures correspond to clusters of lines (or vibrational bands, if rotation is treated separately). In a discrete molecular spectrum with negligible natural linewidths, both structures may be very complex but are still discrete, even if at low resolution the envelope of the absorption looks continuous, and perhaps similar for both types of structure. Thus the term *broadening* is to be avoided here. Otherwise this nomenclature (188) is deliberately similar to the common use of homogeneous (for instance natural lifetime-) broadening and inhomogeneous (for instance Doppler-) broadening, as the mechanisms have some

similarity, the major difference being the discrete or continuous nature of the spectrum.

In order to illustrate these somewhat abstract concepts, Figure 5 shows examples from model calculations (188, 190) and Figure 6 presents two typical "real-life" examples for such structures (188, 191). We concentrate here on the purely vibrational part (inclusion of rotation follows similar lines). Whereas superficially such spectral structures may look similar, particularly when they are blurred in a continuous envelope, there are profound differences. The response to coherent optical excitation is totally different (188; see also "cases Band C" of Ref. 192). There will be "hole burning" in one case when there is none in the other, for instance. At zero Kelvin, for a ground state ensemble in general, there is only homogeneous structure. Most important for the present considerations are, however, the different intramolecular mechanisms giving rise to the structures. Although both types often arise because of the anharmonic interactions between molecular vibrations, inhomogeneous structures, such as the hot band sequence structures shown in Figures 5 and 6, correspond to vibrational modes that can be made separable in some way, whereas the homogeneous structures such as the Fermi resonance structures in Figures 5 and 6 correspond ultimately to nonseparable vibrations and are the signature of intramolecular vibrational redistribution (IVR) and energy flow (194).

# Empirical Observations and Effective Hamiltonian of the CH Stretching-Bending Fermi Resonance

Figure 6b shows a recent example of a multiplet of bands arising from the Fermi resonance between the CH stretching and bending modes. Whereas the existence of such a Fermi resonance has been known for some time (180), only much more recently has this been analyzed systematically and recognized as one of the major pathways of intramolecular energy flow in organic molecules (7, 193–195). "Fermi resonance" refers to an anharmonic resonance between vibrational modes, which have an approximate 1:2 ratio of frequencies, as first correctly interpreted for the spectrum of  $CO_2$  (196). There is nothing special about this particular (1:2) resonance, except, perhaps, its frequent occurrence. Other anharmonic resonances are well known to exist (1:3, 1:4 etc), but only the "Darling-Dennison" (2:2) resonance is traditionally another "named" resonance (the named "Coriolis" resonance is a *rovibrational* resonance).

A careful examination of overtone spectra of the CH chromophore in CHX<sub>3</sub> molecules has resulted in the general picture shown in Figure 7 (7). In place of the CH stretching overtone with quantum number N, one observes a multiplet of N + 1 bands that arise from the close lying stretching  $(v_s)$  and bending  $(v_b)$  levels satisfying

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$$N = \mathbf{v}_{\mathrm{s}} + \frac{1}{2} \mathbf{v}_{\mathrm{b}}.$$

Both the positions and intensities can be reproduced and predicted by a very simple effective Hamiltonian matrix with diagonal elements given by the usual spectroscopic term formula to low order (1, 7)

$$T_n = \sum_j \tilde{v}_j \mathbf{v}_j + \sum_j \sum_{j \ge i} x'_{ij} \mathbf{v}_j \mathbf{v}_j + \sum_j \sum_{j \ge i} g'_{ij} l_i l_j$$

restricted explicitly to CH stretching and bending:

$$H_{\mathbf{v}_{s}\mathbf{v}_{b}\mathbf{l}_{b},\mathbf{v}_{s}\mathbf{v}_{b}\mathbf{l}_{b}}^{\mathbf{n}} = \tilde{v}_{s}'\mathbf{v}_{s} + \tilde{v}_{b}'\mathbf{v}_{b} + x_{ss}'\mathbf{v}_{s}^{2} + x_{bb}'\mathbf{v}_{b}^{2} + g_{bb}'l_{b}^{2} + x_{sb}'\mathbf{v}_{s}\mathbf{v}_{b}.$$
9.

The matrix is block diagonal in the quantum number N, with off diagonal coupling matrix elements within each block defined by a single coupling constant  $k'_{sbb}$ .

$$H_{\mathbf{v}_{s}\mathbf{v}_{b}\mathbf{l}_{b},(\mathbf{v}_{s}-1)(\mathbf{v}_{b}+2)/_{b}} = -\frac{1}{2}k'_{sbb}\left[\frac{1}{2}\mathbf{v}_{s}(\mathbf{v}_{b}-l_{b}+2)(\mathbf{v}_{b}+l_{b}+2)\right]^{1/2}.$$
 10.

The matrix is thus diagonal in the vibrational angular momentum quantum number  $l_b$  to within this approximation. This effective Hamiltonian can be derived in the standard way from spectroscopic perturbation theory (197–199). If this is done, the Fermi resonance coupling constant  $k'_{sbb}$  is given by the cubic force constant  $C_{sbb}$  in the Taylor expansion of the potential in rectilinear normal coordinates  $q_s$  and  $q_b$  ( $q_b^2 = q_{b1}^2 + q_{b2}^2$ , for the degenerate bending vibration)

$$\frac{V}{hc} = \frac{1}{2}\omega_{\rm s}q_{\rm s}^2 + \frac{1}{2}\omega_{\rm b}q_{\rm b}^2 + C_{\rm sbb}q_{\rm s}q_{\rm b}^2 + C_{\rm ssbb}q_{\rm s}^2q_{\rm b}^2 + \cdots$$
 11.

Table 1 summarizes a collection of results for Fermi resonance coupling constants and force constants, derived as described below (200). Although the identification  $k'_{sbb} \simeq C_{sbb}$  would have been the accepted spectroscopic procedure for several decades, and certainly *qualitatively* adequate, this is clearly not correct quantitatively. As first pointed out in (7), other interpretations and definitions of the Fermi resonance coupling constant

*Figure 5* Illustration of "homogeneous" and "inhomogeneous" spectral structures (188). (a) Schematic representation indicating transitions and levels as well as the absorption structure,  $\sigma$ , which may be similar for both types. Note that the role of upper and lower levels could be inverted (denoted "reverse"), resulting in temperature dependence for the homogeneous structure or an emission band structure (30). (b) Model calculation for inhomogeneous structure of the CH-stretching band in (CF<sub>3</sub>) C-C=C-H (discrete structures under the continuous envelope, Ref. 188). (c) Model calculation for discrete homogeneous structure (envelope not drawn). The coupling scheme for the upper level shown in the insert corresponds to two local states coupled to a dense spectrum (Ref. 190; see also section on local modes).





Figure 6 Examples of experimently observed spectral multiplet structures: (a) Inhomogeneous structure arising from hot band sequence transitions in the N = 3 CH-stretching overtone of CF<sub>3</sub>CCH. The *Q*-branch maxima indicate vibrational structure, apart from the *P*, *Q*, *R* rotational envelope (188). (b) Inhomogeneous structure arising from the N = 3 CHstretching Fermi resonance multiplet in <sup>13</sup>CF<sub>3</sub>H (191). Four *Q*-branch maxima indicate vibrational structure.

are possible, and, indeed, warranted. The "exact" interpretation has been discussed in (201), in the framework of the Born-Oppenheimer approximation, at least. This requires the solution of the Schrödinger equation on the complete Born-Oppenheimer potential (in nine dimensions for CHX<sub>3</sub>)



*Figure 7* Fermi resonance multiplets for the CH-stretching overtone transitions in CF<sub>3</sub>H. For the overtone with quantum number N one has N+1 vibrational bands, shown as sticks with points (intensity proportional to height, numbers give polyad positions in cm<sup>-1</sup>). [Reproduced by permission from J. Chem. Phys. (7).]

molecules) and evaluation of the computed optical spectrum by the same effective Hamiltonian as discussed above for experimental spectra. The resulting (theoretical) spectroscopic coupling constant  $k'_{sbb}$  would be directly comparable to the experimental result. Such calculations have not yet been carried out but several other, approximate, models have been proposed, discussed in the following chapters.

First, however, we shall mention here one conceptually interesting interpretation, which helps to differentiate between anharmonic couplings giving inhomogeneous structure and those giving homogeneous structure, both in alkylic and acetylenic CH spectra (202, 203). In this interpretation the diagonal part of the effective Hamiltonian, Eq. (9), is obtained from a vibrationally adiabatic  $\hat{H}_0$  with

$$\hat{H}_{0}\psi_{nm}^{0} = E_{nm}^{0}\psi_{nm}^{0}$$
  
$$\psi_{nm}^{0} = \phi_{n}(\mathbf{b}, \mathbf{s})\xi_{nm}(\mathbf{b}).$$
 12.

The  $\phi_n$  are solutions of the "clamped bending" Schrödinger equation:

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Spectroscopic constants and force constants for the Fermi resonance in CHX, molecules Table 1

	CH	$[D_3^4]$	CHF	a <sup>E</sup>	CHCI <sub>3</sub> <sup>6</sup>	CHBr <sup>ad</sup>	CH(CF <sub>3</sub> ) <sup>6</sup>
Constant	exp	ab initio	exp	ab initio	exp	exp	exp
$\tilde{v}_{\rm s}^{\prime}/{ m cm}^{-1}$ $\tilde{v}_{\rm c}^{\prime}/{ m cm}^{-1}$	3048 1292	3148 3126	3086	3126	3096	3110	3053
$x_{ss}^{\prime}/cm^{-1}$	-58	07CI	0/ C1 64	-67	1221 65	1148 66	1353 58
$x_{bb}^{(bh)}/cm^{-1}$	-4.5 - 22	-5.0 34	5.6	-7.5	-6.5	-5.0	1.2
$g'_{\rm bb}/\rm cm^{-1}$	2.6	3.8	6.7 7.6	34 11.5	26 7.8	-21 3.2	-22 19
$ k_{\rm sbb} /{\rm cm}^{-1}$	<b>30±15</b>	31	$100 \pm 10$	66	85±15	$75 \pm 30^{1}$	$70 \pm 15$
$egin{array}{l} C_{ m sbb}/ m cm^{-1} \ C_{ m sbb}/ m cm^{-1} \ F_{ m sbb}/ m cm^{-1} \ F_{ m sbb}/ m cm^{-1} \ A_{ m -1} \ F_{ m sbb}/ m cm^{-1} \ A_{ m -2} \end{array}$	$97\pm 50$ - 50 - 8809 - 73,627	$140 \pm 15 \\ -78 \\ -12,849 \\ -47,252$	187 - 92 5268 77,424(fix) <sup>i</sup>	187 - 85 - 20,228 - 77,424	265 <sup>f</sup> -116 -10,489 0(fix)	245 -94 -2686(0) <sup>\$</sup> 0(fix) <sup>j</sup>	115 - 50 - h
<sup>a</sup> Experiment: Refe <sup>b</sup> Experiment: Refs <sup>c</sup> Refs. (50, 218, 218, 21 <sup>d</sup> Refs. (132, 191, 21 <sup>d</sup> Refs. (50, 188, 22, 2 <sup>c</sup> Refs. (50, 188, 22 <sup>f</sup> An ab initio calcu	s. (12, 147, 148, 20) s. (7, 20). Theory: 1 9, 208). For <sup>1,5</sup> CH, 21, 226). 0.	0, 201). Theory: Refs. Refs. (50, 200). For <sup>11</sup> Cl <sub>3</sub> see Ref. (191) (als	(50, 200, 201, 217). CHF <sub>3</sub> see Ref. (191) ( <i>i</i> so for F <sub>tab</sub> and F <sub>stbb</sub> ).	also for $F_{\rm shb}$ and $F_{\rm sht}$	). (		

<sup>b</sup> Because of the delocalized nature of the bending vibration in this molecule, the derivation of internal coordinate force constants for this molecule would have little <sup>6</sup>One may constrain  $F_{sbh} = F_{ssh} = 0$  and still get a good fit to experiment (191). For the definition of the force constants  $F_i$  see Refs. (132, 209).

<sup>1</sup>The agreement between experiment and ab initio theory remains poor if F<sub>ssb</sub> is floated and if corrections to the model are applied, thus indicating limitations of the or no physical meaning (50).

<sup>3</sup>The best current estimate for  $|K_{shb}|$  is near 55 cm<sup>-1</sup>; a good set of force constants is also  $F_{sb} = 21,700$  cm<sup>-1</sup> Å<sup>-1</sup>;  $F_{shb} = -244,000$  cm<sup>-1</sup> Å<sup>-2</sup> (267), the sign of the F being undetermined, even. model and the F derived.

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$$\hat{H}(\mathbf{b},\mathbf{s})\phi_n(\mathbf{b},\mathbf{s}) = V_n(\mathbf{b})\phi_n(\mathbf{b},\mathbf{s}).$$
13.

The  $V_n(b)$  are effective potentials for the bending coordinate for each quantum number  $n = v_s$  of the stretching vibration. The adiabatic solution is given by introducing the kinetic energy  $\hat{T}_b$  in the bending coordinate

$${\hat{T}_{b} + V_{n}(b)}{\xi_{nm}(b) = E_{nm}^{0}\xi_{nm}(b).$$
 14.

Because of the dependence of  $V_n(b)$  upon the stretching state, there is a change of bending frequency with stretching excitation:  $\tilde{v}_b(\text{eff}) = (\tilde{v}_b + x_{sb}v_s)$ . This mixed anharmonicity  $x_{sb}$  on the *diagonal* of  $H^N$  precisely leads to the inhomogeneous multiplet structure shown as an example for CF<sub>3</sub>CCH in Figure 6. It does *not* lead to efficient vibrational redistribution. In this interpretation, such redistribution is entirely due to vibrationally nonadiabatic coupling of the  $\psi_{nm}^0$ . While these concepts are attractive to explain the observed phenomena qualitatively, we now turn to some models for which more quantitative results are available.

# Curvilinear Internal Coordinate and Rectilinear Normal Coordinate Models for the Fermi Resonance

Following our first analysis (7a), which drew attention to the ambiguity in the interpretation of the Fermi resonance coupling, the theoretical analysis of the Fermi resonance has found considerable interest. No "exact" calculations as defined in the previous section (201) have been carried out, but several more or less successful approximate, quantitative models have been proposed. We now discuss the merits and limitations of these models both in relation to experiment and to ab initio theory.

One type of model is based upon an idea of Sibert et al (204, 205), who proposed to formulate the Fermi resonance problem in curvilinear, internal coordinates, with the hope that in this representation the Fermi resonance coupling constant might be deduced from the *G*-matrix alone, without reference to the anharmonic coupling potential. Of course, the coupling potential can still be introduced. This idea has been followed up by more detailed work (206–213; see also 41, 191, 211). The work has been directed to establish a relation between the observed anharmonic constants (in particular  $k'_{sbb}$ ) and the potential and *G*-matrix for the Fermi resonance. One can distinguish simple, closed analytical expressions for this relation and more complicated results based on variational calculations using the internal coordinate Hamiltonian. The latter can be compared to experimental spectroscopic constants (such as  $k'_{sbb}$ ) by a similarity transformation to the form of the effective Hamiltonian. It is not possible here to repeat in detail the often lengthy formulations of the various models,

but we shall summarize the main results (see also, in particular, the discussions and conclusions of Refs. 50 and 200a).

- 1. The internal coordinate models give a reasonable *qualitative* picture of the Fermi resonance and some of the models (e.g. 209) can be fitted to experiment with an accuracy similar to the effective Hamiltonian.
- 2. The neglect of potential coupling (204, force constants  $F_{sbb}$  and  $F_{ssbb}$  in Table 1) gives always poor results, quantitatively, except for CHBr<sub>3</sub>, where it gives roughly satisfactory results (191, 267).
- 3. Comparison with accurate ab initio calculations for CHD<sub>3</sub> and CHF<sub>3</sub> suggest that the anharmonic force constants derived even from the most advanced (variational) internal coordinate model (209) do not compare well with ab initio force constants. Presumably, the differences arise mostly from limitations of the internal coordinate model, including ambiguities in the choice of coordinates for the potential.
- 4. The most serious limitation of all internal coordinate models proposed so far is the neglect of coupling to the motions of the heavy atom CX<sub>3</sub> frame. Another problem arises from the limited validity of the approximate expansions of the kinetic energy operator (212, 213).
- 5. A final serious drawback of the internal coordinate models is the dependence of the force constants derived from experiment upon the often poorly known, exact structural parameters of the molecules (191).

A more complete treatment has been based on rectilinear normal coordinates but using a polar coordinate representation of the potential (200). This treatment includes an exact representation of the kinetic energy operator and some coupling to the motion of the heavy nuclei by means of the definition of the normal coordinates. This model leads to satisfactory agreement between experiment and ab initio theory, both for the effective Fcrmi resonance constant  $k'_{sbb}$  and the large anharmonic force constants (in normal coordinates)  $C_{sbb}$  and  $C_{ssbb}$  as can be seen from Table 1. The model is able to predict isotope effects about as well as the other models even if further simplifications are made (191). The neglect of explicit coupling with the other modes thus does not seem to be too serious at this level of approximation. Full calculations in nine dimensions for CHD<sub>3</sub> have been presented recently (214), but it is not clear whether these are satisfactory in comparison with experiment and ab initio theory (200).

In the comparison of rectilinear and curvilinear coordinate models it has sometimes been stated that the latter are better in the context of the Fermi resonance (41, 208). This is certainly incorrect as far as quantitative validity goes. The misunderstandings arise from the limitations of the *traditional* (rectilinear coordinate) approach (197). These limitations arise from the use of perturbation theory and an inadequate Taylor expansion of the potential, as clearly demonstrated in the case of  $CHD_3$  (200, 215). They do not arise from the choice of coordinates. Indeed, a variational treatment on an adequate potential following the rectilinear normal coordinate expansion is perfectly successful and at present the only satisfactory solution. On the other hand, the drawbacks, which we find now for the internal coordinate models, do not arise from the choice of coordinates per se but rather from some secondary approximations. The CHQ-Hamiltonian (209) seems to be best approximation in the internal coordinate is immaterial. In any case, the CH stretch-bend Fermi resonance provides now a test case, where a good understanding ranging from ab initio potentials to empirical fits of high overtone spectra at high resolution has been obtained. This proper understanding has provided surprises beyond traditional spectroscopic analyses and is of crucial importance for time dependent intramolecular dynamics (216).

# The Influence of Molecular Symmetry and Structure on Anharmonic Resonances

The local CH dynamics is characterized by three degrees of freedom. In CHX<sub>3</sub> molecules approximate symmetry introduces an approximate (!) good quantum number  $l_{\rm h}$  for the vibrational angular momentum of the degenerate bending vibration. Thus, effectively only two strongly coupled modes exist; this results in the number of coupled levels increasing as N+1or in a density of coupled states proportional to energy. If the  $C_{3y}$  symmetry is removed,  $l_{\rm b}$  is no longer a good quantum number and we have a subsystem of three modes (stretching and two bending vibrations) strongly coupled by Fermi and Darling-Dennison resonances. The density of coupled states increases proportional to  $E^2$ . This is beautifully borne out by experiment (222, 223). The spectra in the molecules CHXY<sub>2</sub> with X, Y =Cl.  $CF_3$ , F, D have been analyzed with a model similar to the one for CHX<sub>3</sub> (but more complex) and algorithms developed by the Zürich group (223) in several publications (208, 222-225). The order of magnitude of the couplings is similar to the one shown in Table 1 for symmetric tops, with Fermi resonance constants of the order of up to 100 cm<sup>-1</sup> and a number of further couplings. The influence of symmetry on redistribution is thus well established.

Another aspect is the relation between *structure and dynamics*. If the C=CH dynamics at an acetylene group is considered, the strong Fermi resonance disappears because of the low bending frequency: The large CH stretch bend anharmonicity is still present, but it is manifest through *inhomogeneous* structure, as already shown in Figure 6 (188, 189). Investigations on several substituted acetylenes have shown that both fun-

damental and overtone spectra are characterized by a well separated CH stretching vibration, coupled through weak interactions to the molecular heavy atom frame (83, 115, 188, 189, 202, 227, 228). The case of HCN (136, 229) may be also quoted in this context. An intermediate situation arises in CH at an  $sp^2$  carbon atom, where the out of plane bending vibration is of low frequency and effectively decoupled, whereas the in plane CHbending vibration enters a strong Fermi resonance with the stretching vibration. This has been demonstrated for CD<sub>3</sub>CHO (267) and may be the mechanism responsible for the broad CH overtones in benzene (134). The observation of narrow structures in lower CH-overtones of benzene in supersonic jet experiments (169) does not contradict the possibility of strong anharmonic couplings (and fast IVR), because no analysis of the weak substructures was carried out. Despite the heroic experimental effort, the benzene spectra remain poorly understood. Further effort, particularly in the analysis, is necessary. The situation is better for  $NH_3$ , where a detailed analysis up to high overtones of the NH stretching vibrations has been possible (165). An analysis has also been presented recently for  $CH(CD_3)_3$  and some further partially deuterated alkynes and alkenes (230) and for CH<sub>3</sub>Cl (231).

The examples discussed above all refer to very strong, dominant anharmonic couplings. There is, of course, an enormous amount of data on weaker anharmonic couplings and "perturbations" in spectra of small polyatomic molecules (for a discussion of an example CH<sub>3</sub>Br see Ref. 232). These have generally been analyzed in terms of effective Hamiltonians. Recent experimental advances should also further a thorough understanding of weak anharmonic couplings. Examples are the supersonic jet FTIR and laser spectroscopy of CF<sub>3</sub>I (85, 88) and CHF<sub>3</sub> (17, 82, 233). The weak couplings tend to mix all vibrational modes. CHF<sub>3</sub> is a nice example for the separation of time scales arising from the disparity in the large couplings within the CH stretching and bending modes (100 cm<sup>-1</sup>) and between these modes and the frame (at least an order of magnitude smaller). This point has been discussed semiquantitatively early on (193–195) and is now well confirmed (17, 217, 233). It is the basis for mode selective IVR in a time dependent view.

# Time Dependent Aspects of Vibrational Motion

One goal of the spectroscopic analysis of vibrational motion is to elucidate fast time dependent processes in polyatomic molecules and their influence on chemical reactivity. Early analyses of the broad overtone band shapes in benzene in terms of a subpicosecond relaxation of the local CH stretching excitation may, *perhaps*, be correct (134, 194). However, to this date these spectra have not been analyzed in terms of the contributions from molecular states and wavefunctions and thus we cannot claim an understanding of the primary processes after local excitation in benzene, although some theoretical models have been proposed (134, 204–206, 234).

The situation is much more favorable for the interactions in the alkyl CH chromophore, where we have now a satisfactory understanding of the local Hamiltonian governing the short time dynamics in the isolated system, say, for the wavefunction  $\psi$  by the equation

$$\psi(t) = \exp\left(-2\pi i \hat{H} t/h\right)\psi(0).$$
15

Time dependent calculations have been reported ranging from level populations (7a, 165, 188, 190, 195, 222, 223) to detailed evaluations of molecular probability densities in space (216). Instead of showing the more complex examples here, we present results of calculations for a simplified description of the relaxation of molecular entropy to equilibrium, after excitation of CHF<sub>2</sub>Cl in the N = 6 overtone of CH stretching (223). From Figure 8 one sees that relaxation, indeed, occurs and that the entropy reaches about 80 to 90% of its microcanonical equilibrium value for the subset of three coupled oscillators on a time scale of 200 femtoseconds. Although details depend upon the definition of entropy used (two different ones are shown in the figure), the main result is rather insensitive to this. We may thus consider this as confirmation of mode selective relaxation and the second law for isolated molecules on a fully dynamical level (235).



*Figure 8* Time dependent entropy for a subset of three coupled oscillators after pure CHstretching excitation in CHClF<sub>2</sub> with six quanta at t = 0. [Two slightly different definitions of entropy are shown;  $S_{max}$  refers to a microcanonical ensemble of three oscillators in this energy range, neglecting the other vibrational modes by restricted equipartition (223).]

# LOCAL MODES AND INFRARED CHROMOPHORES

In molecules with several symmetrically equivalent bonds, for instance CH<sub>4</sub> or C<sub>6</sub>H<sub>6</sub>, the ordinary "textbook" approach would be to define delocalized, symmetrized normal vibrations as a starting point (1-3, 236). An alternative is to start from the localized bond vibrations and introduce the kinetic energy coupling (and symmetrization) at the end. This is the basis of "local mode theory," with a history of about 50 years as a quantitative quantum mechanical theory (237, 238), and has become very popular (perhaps overly so) in recent years. Correspondingly this field has been extensively reviewed (58, 61, 239, 240); such reviews have emphasized either a more phenomenological description of experimental findings or the pure theory of classical and quantum dynamics of coupled local modes. Some complementary thoughts on concepts and results that have found less attention are presented here. In addition to the "normal mode" and "local mode" vibrational states, "hyperspherical modes" (241-244) and "global vibrational states" (190) have been introduced as new concepts, the latter being one starting point for the growing field of statistical interpretations of spectra (190, 245-247).

## Chromophore Intensity and Local Modes

One way to view local modes is to focus on their property as "vibrational chromophores" that can be empirically defined by a group in a molecule giving rise to absorption in well-defined frequency ranges. The band strength arising from such a chromophore may be spread over a considerable frequency range; this implies that there need not be any long time localized motion associated with the localized chromophore (one may, of course, have delocalized chromophores, which are not discussed here). The local mode *chromophore concept* (193, 248) can be eminently useful to characterize the interaction of molecules with infrared radiation, say, in laser chemistry or analytical applications. The empirical goal is to find regularities in the band strength G [expressed as integrated molecular absorption cross section  $\sigma(\tilde{v})$ ]:

$$G = \int \tilde{v}^{-1} \sigma(\tilde{v}) \, \mathrm{d}\tilde{v}.$$
 16.

If the chromophore property can be associated with a localized vibrational motion (in one or more dimensions), G can be related to the electric dipole transition moment (in cgs Debye units, add  $4\pi\epsilon_0$  in the denominator of Eq. 17a for complete SI system):

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$$G = \frac{8\pi^3}{3hc} |\langle \mathbf{v}_f | \mu | \mathbf{v}_i \rangle|^2$$
 17a.

$$= 41.624 \left(\frac{|\langle \mathbf{v}_f | \boldsymbol{\mu} | \mathbf{v}_i \rangle|}{\text{Debye}}\right)^2 \text{pm}^2$$
 17b.

$$=\frac{c^2}{8\pi v^3}A=\frac{h}{c}B.$$
 17c.

This equation is written as a practical mixture of SI units for G and molecular cgs units (Debye), with initial and final vibrational quantum numbers  $v_i$  and  $v_j$  and the Einstein coefficient for spontaneous emission, A. There has been some systematic experimental work on the question of characterizing bandstrengths empirically (218, 238, 248–252). The main conclusions that have emerged can be summarized as follows:

- 1. Local vibrations carry a well-defined fundamental oscillator strength, which depends upon the chemical environment in terms of group additivity rules (248).
- 2. Band strengths from similar, but well-separated groups in molecules are simply additive (252).
- 3. Overtone band strengths of the CH group seem to be additive even if the groups are not well separated, and they seem to be increasingly independent of neighboring groups as the overtone quantum number is increased (249, 250).

These conclusions, when further confirmed, will obviously give rise to a number of interesting potential applications. The overtone band strengths of local modes have also been analyzed in terms of local dipole moment functions. Most work has dealt with simple, one-dimensional electric dipole moment functions of the type introduced by Mecke and coworkers (238, 240, 253)

$$\mu(\mathbf{r}) = \operatorname{const.} \mathbf{r}^{\mathrm{m}} \exp\left(-\alpha \mathbf{r}\right).$$
 18.

Recently extensions to dipole functions in several dimensions (for the local group) have been investigated (254). The preliminary conclusions from these investigations were that in comparison with experimental band strengths and ab initio dipole moment calculations, these representations were satisfactory, but not perfect. Much further work would be desirable in the systematic characterization of chromophores in the infrared.

# Time Dependent Local Modes

Although the concept of localized dipole absorption properties has a solid empirical foundation, the question of localized dynamics (on long time

scales) associated with local modes is more complex. It would be of considerable interest in relation to the theory of unimolecular reactions (31) and laser chemistry (22). If local modes existed as long lived local excitations at high energy, they might be used for various schemes of mode selective chemistry. The question of local mode time dependence has been particularly clearly discussed in the work of Child & Lawton on H<sub>2</sub>O, which is also the basis of subsequent work from the Oxford group (255, 256). Briefly, the prediction for water (or a general  $R_nXH_2$  molecule) would be that certain vibrational eigenstates occur in closely degenerate pairs (splitting  $\Delta E$ ), such that symmetric and antisymmetric combinations of the eigenstates correspond to localized excitations ( $v_1 = n$ ,  $v_2 = 0$ ) and ( $v_1 = 0$ ,  $v_2 = n$ ) with *n* quanta in the bond stretching mode 1 or 2. The energy flow between the two bond vibrations would be periodic, with a (half period) transfer time

$$t_{\rm t} = \tau/2 = h/2\Delta E. \tag{19}$$

Splittings predicted for H<sub>2</sub>O are about 100 cm<sup>-1</sup> for the fundamental (n = 1), 4 cm<sup>-1</sup> for n = 4 (near 14,000 cm<sup>-1</sup>), and 0.6 cm<sup>-1</sup> for n = 5 (near 17,000 cm<sup>-1</sup>). This corresponds to transfer times of 4 ps at n = 4, 30 ps at n = 5, and even 30 ns at n = 8 (256).

The critique of this model suggested (190) that according to the scheme shown in Figure 5 for the "homogeneous structure," coupling with the other modes (and rotation) through Fermi resonance and rovibrational interactions will destroy the close degeneracies, the regularity of the motion, and long lived local excitations. Based on this remark (190) and further ideas along these lines (M. Quack, unpublished), recent work using an extension of the original CHQ Hamiltonian (209) has, indeed, shown the importance of the Fermi resonance coupling for the local mode dynamics in H<sub>2</sub>O and CX<sub>2</sub>H<sub>2</sub> (257; the CH<sub>2</sub>X<sub>2</sub> project had been partly assigned to L. Halonen in a collaborative project within the Zürich group started in 1985). There had also been experimental evidence of a dominant Fermi resonance interaction in  $CH_2X_2$  systems that would destroy any long lived local excitations (258; M. Quack and N. Spirig, unpublished). For H<sub>2</sub>O there exist very accurate recent variational vibrational calculations to energies above the n = 6 overtone (259). In the range of the n = 5 overtone. the closest symmetric-antisymmetric degeneracy observed is  $5 \text{ cm}^{-1}$  and in the region of the n = 6 overtone it is 1 cm<sup>-1</sup>, in clear contradiction to the simple local mode model (256). Indeed the level spacings in this energy range were analyzed in terms of a statistical Wigner distribution (259), in agreement with the qualitative suggestion made in (190). Although the new calculations on  $H_2O$  (259) provide a benchmark for this type of problem, the general question of the existence of localized states remains

of interest. One must recognize that in considering these very small energy splittings numerical errors may still be significant.

# Some Remarks on the History of the Local Mode Model

The history of the local mode model has some striking peculiarities that have largely escaped notice and that we shall briefly mention. One may distinguish roughly five phases in the development of the concept. In the early days of spectroscopy the idea of IR-absorption localized in certain parts of molecules was clearly recognized (260) and with the advent of quantum mechanics a local CH Morse oscillator was introduced to explain overtone absorptions (261). In the second phase, R. Mecke and coworkers between about 1930 and 1950 pursued an intense effort resulting in numerous publications (e.g. 237, 238, 262). Overtone spectra were extensively investigated experimentally and analyzed in terms of a quantitative theory that contained most aspects of "modern" local mode theory. Mecke discussed the anharmonic decoupling of the local modes and the relation to normal mode theory as well as electric dipole moment functions and overtone intensities, including such "modern tricks" as effectively using the Morse coordinate  $y = 1 - \exp(-ar)$  (200). Some of the theoretical results have been reproduced even after 1980 (including great similarities, but without reference to the original). Thus the third phase "rediscovery" is characterized by neglect of the early work on local mode theory, perhaps in part due to the overwhelming fashion of normal mode treatments between 1950 and 1970. After 1968, local mode theory was rediscovered (263), presumably the concept was still vaguely alive, and slowly redeveloped (264), which then characterized phase four, the "new fashion" of local mode theory. Until recently, including several reviews (58, 61, 239, 240), Mecke's work was not given credit, although attention had been drawn to it (190, 250) and the work is referenced in Herzberg's books (1). The interesting correlations among bond lengths, bond energies, and "local" vibration frequencies introduced another interesting concept related to local modes (265). Of the final, fifth, phase of maturity of the local mode theory we just mention recent work showing, to some extent, the equivalence of local mode and normal mode theory (266).

The purpose of this short historical review is not at all to provide estimates of merit—for which a much longer discussion would be necessary. Rather, we remind ourselves that considerable inspiration can be drawn from reading the original papers, even in the older or sometimes less well-represented literature, in which often the concepts of modern research were introduced. Likewise, a general aim of this review is to view timeliness by content, rather than by date.

# CONCLUSIONS AND OUTLOOK

The interplay of advances in experiment and theory has provided new insight in the spectra and dynamics of coupled vibrations in molecules. Perhaps the most important advance has been the new understanding achieved, far beyond traditional methods of spectroscopy, of the relation among the observed high resolution spectra of excited states, the anharmonic potential functions, and the time dependent vibrational motion governed by these. Important effects, such as the dominant effective Fermi resonance coupling  $k_{sbb}$  in CH chromophores, and their nontrivial relation to the potential are now understood quantitatively, even *ab initio*, but this field is far from being closed—quite to the contrary, new avenues have just been opened. The traditional theory of classical harmonic motion and nonlinear anharmonic resonance dynamics that retains just a few terms in the Taylor expansion of the coupling has to be replaced. In the future this will have a profound influence on our understanding of intramolecular dynamics in unimolecular reactions, laser chemistry, or the motion of biopolymers—all governed by the quantum dynamics of anharmonic, coupled vibrations.

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