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Coordination Chemistry Reviews 230 (2002) 213–224

COORDINATION
CHEMISTRY REVIEWS

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Infrared vibrational band shapes in excited states

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Received 19 September 2001; accepted 7 November 2001

Dedicated to Dick Stufkens, friend and colleague for many years

Contents

Abstract

This article describes the behaviour of the shapes of the IR bands of coordination compounds on electronic excitation. Broadening on excitation is frequently, but not invariably, observed; any broadening is the result of a subtle interplay of the properties of the vibrational mode, the excited state and the solvent. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Infrared; Vibrational; Excited states; Band shapes

1. Introduction

Some years ago Hamaguchi [1,2] drew attention to the fact that Raman bands of molecules in electronically excited states tend to be broader than the corresponding ground state bands; since then there have been many papers which include discussion of these features [3–6]. More recently, Clark et al. [7] pointed out a similar effect in the ν(CO) IR bands of coordination compounds, with the increase in width being a sensitive function of the nature of the excited state and of the solvent. Chen and Palmer [8] also drew attention to the fact that "broader bandwidths are commonly observed

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PII: S0010-8545(01)00471-4

for ν(CO) IR bands in the MLCT excited states of metal carbonyl complexes although the origin of this phenomenon is not clear''. Of course, information on the nature of excited states, deduced from vibrational spectroscopy, concentrates on the frequencies and intensities of the vibrational bands, but the largely ignored band shapes can also provide important details. This chapter concentrates on what influences the IR band shapes in the excited states of coordination compounds, and what can be deduced from observations on these shapes.

We start, in Section 2, by reviewing what determines the shapes of vibrational bands in the *ground* state. This introduces the concepts of: Section 2.1 the Fourier Transform relationships between the frequency (spectral) domain and the time domain; Section 2.2 correlation functions and their connection with IR and Raman spectra; Section 2.3 homogeneous versus inhomogeneous broadening; Section 2.4 dephasing processes, leading to the conclusion that for this review the 'pure' dephasing mechanism is the most important. This is followed, in Section 2.5, by consideration of a relevant study which notes that the Raman bandwidths of organic radicals in solution are broader than the bandwidths of the parent molecules.

Since most excited state IR spectra of coordination compounds involve metal ν(CO) bands, it is important to consider the spectroscopic behaviour of metal carbonyls in the electronic *ground* state. This is done in Section 2.6, confining comments to molecules in solution at room temperature (r.t.).

Section 3 is concerned with IR bandwidths in the excited states of coordination compounds. We first consider (Section 3.1) some preliminary observations—building on the first experiments on the ν(CO) spectra in excited states—in which bandwidths in excited states were first explicitly investigated. Section 3.2 provides a brief survey of the literature where it seems possible to make some bandwidth comments, based on the appearance of published spectra. This includes both metal C–O, metal C–N and other vibrations.

Section 4 summarises these observations and attempts to make some general conclusions.

In this article, we shall only consider molecules in solution near r.t. Furthermore we shall ignore any complications from instrument lineshape; this is really for two reasons: many of the published spectra illustrate 'difference' spectra between ground and excited state and hence the contribution to the band shape from the instrument is the same in both states; many excited state spectra have been recorded 'point-by-point' using IR lasers where the instrument line shape contribution is essentially zero (although there are subtle points about the definition of 'resolution').

2. Ground state vibrational bandwidths

This topic has recently been reviewed [9] so only an outline of the important points will be presented here.

2.1. Fourier transform relationships

The shape of a vibrational band is intimately connected with the underlying dynamics in solution by the Fourier Transform (FT) relationships:

$$\Phi(\nu)=\int_{-\infty}^{+\infty}F(t)\mathrm{e}^{-2\pi i\nu t}\mathrm{d}t \qquad F(\nu)=\int_{-\infty}^{+\infty}\Phi(\nu)\mathrm{e}^{2\pi i\nu t}\mathrm{d}\nu$$

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}F(t)\mathrm{e}^{-i\omega t}\mathrm{d}t \quad F(t)=\int_{-\infty}^{+\infty}I(\omega)\mathrm{e}^{i\omega t}\mathrm{d}\omega$$

Thus the spectrum (i.e. plot of $\Phi(\nu)$ against ν or $I(\omega)$ against ω) is the FT of a time-dependent function $F(t)$ and vice versa. Suppose $F(t)$ has an exponential decaying form (quite common), e.g.:

$$F(t)=\mathrm{e}^{-|t|/T_2}$$

where $|t|$ represents the modulus of t, and T_2 is chosen for reasons that will be obvious shortly, then the FT of $F(t)$ is:

$$\Phi(\nu)=\int_{-\infty}^{+\infty}\mathrm{e}^{-|t|/T_2}\mathrm{e}^{-2\pi i\nu t}\,\mathrm{d}t=\frac{2T_2}{(2\pi T_2\nu)^2+1}$$

which is a Lorentzian shaped band of FWHM (full width at half maximum intensity) equal to $1/\pi T_2$ Hz ($=2/T_2$ rad s^{-1}). Thus, if T_2 is 10 ps, the Lorentzian has a FWHM of 3.2×10^{10} s^{-1} $\sim$1 cm^{-1}. If $F(t)$ has different decay properties then the FT gives a band of a different shape; for instance a Gaussian decay gives rise to a Gaussian band. There are actually considerable subtleties in these relationships, which are outside the scope of this chapter (see [9,10]).

Thus, in principle, we can either use the observed spectrum to obtain information about the underlying system dynamics, or attempt to calculate the features of the underlying dynamics and hence predict the spectrum.

2.2. Correlation functions

It was Gordon who introduced a method of describing the nature of $F(t)$ by using *correlation functions* [11]. The *auto*correlation function ($C(t)$) of some property A, assuming we start at $t=0$, is given by:

$$C(t)=\langle A(0)A(t)\rangle$$

(usually normalised by dividing by $[A(0)]^2$)

where the brackets imply the ensemble average (i.e. over all molecules). Thus $C(t)$ describes how long property A persists until it is averaged out by the motion of the molecules in the system. It will eventually become zero, and the (normalised) *correlation time* is defined by:

$$\tau_c = \int_0^{\infty} C(t)\mathrm{d}t$$

The spectrum and correlation function are related by:

$$\Phi(\nu) = \int_{-\infty}^{+\infty} C(t)\mathrm{e}^{-2\pi i\nu t}\mathrm{d}t$$

i.e. in the FT equations $F(t)$ becomes $C(t)$. The question is how $C(t)$ is connected to the usual vibrational spectroscopic properties such as dipole moments and polarisabilities. Gordon showed that for the IR spectroscopy of isotropic samples, the autocorrelation function is:

$$C_{\mu}(t) = \langle \boldsymbol{\mu}(0)\boldsymbol{\mu}(t)\rangle$$

where μ is the transition dipole moment. If the coupling between vibration and rotation is small:

$$C_{\mu}(t) = C_{1r}(t) + C_{v}(t)C_{1r}(t)$$

The first term ($C_{1r}(t)$) involves pure rotation. The second term involves the product of the rotational term and a vibrational term ($C_v(t)$). The spectrum is given by the FT of this correlation function:

$$\Phi(\nu) = \mathrm{FT}\{C_{\mu}(t)\} = \mathrm{FT}\{C_{1r}(t)\} + \mathrm{FT}\{C_{v}(t)C_{1r}(t)\}$$

The first term gives the pure rotation spectrum $\{\Phi_{1r}(\nu)\}$, which, if $C_{1r}(t)$ decays exponentially, will be a Lorentzian. The second gives the vibrational part modified by the rotation $\{\Phi_{v,1r}(\nu)\}$. It is worth pointing out that the FT of a product of two functions is the convolution of the FTs of each component, i.e. in the present case:

$$\Phi_{v,1r}(\nu) = \mathrm{FT}\{C_{v}(t)\ C_{1r}(t)\} = \Phi_{v}(\nu)^{*}\Phi_{1r}(\nu)$$

where the asterisk represents the convolution. It is only if each contribution, $C_v(t)$ and $C_{1r}(t)$, decays exponentially will the resulting band shape be a Lorentzian with overall FWHM equal to the sum of the FWHM of each component; in other words only then will the contributions from $C_{1r}(t)$ and $C_v(t)$ be additive.

The above describes IR spectroscopy. There are of course equivalent equations for Raman bands where the terms involve polarisabilities (see [9–11]).

2.3. Inhomogeneous and homogeneous broadening

Before discussing in more detail the factors influencing the band shape, we must first consider the problem of *homogeneous* and *inhomogeneous* contributions to the bandwidth. The question is rather subtle and is really best considered using the Kubo model [12] whose approach can be simplified as follows. Suppose a molecular vibration is perturbed by the environment so as to fluctuate over a variety of values, but with some mean value ω_0:

$$\omega(t) = \omega_0 + \delta\omega(t)$$

(ω, rather than ν, since this was Kubo′s notation)

where the mean of $\delta\omega$ is zero.

The modulation amplitude, Δ, of the perturbation is defined by:

$$\langle[\delta\omega(t)]^2\rangle$$

The correlation function of the modulation is defined by:

$$C(t) = (1/\Delta^2)\langle\delta\omega(t)\delta\omega(0)\rangle \text{ (note : this is normalised)}$$

and the correlation time, τ_c, by:

$$\tau_c = \int_0^{\infty} C(t)\mathrm{d}t$$

Thus the correlation time is a measure of the speed of the modulation.

It is the relative values of Δ and τ_c that are of importance. If the fluctuation is ‘slow’ ($\Delta\tau_c \gg 1$), then the spectrum will appear as the superposition of the variety of perturbed frequencies. This is ‘inhomogeneous’ broadening and, usually, but *not* invariably, the overall band shape will be Gaussian, and the FWHM will be $\sim\Delta$ rad s^{-1}. If the fluctuation is ‘fast’ ($\Delta\tau_c \ll 1$), then ‘motional narrowing’ occurs, and the band becomes, usually, Lorentzian, with a bandwidth of $\Delta^2\tau_c$ rad s^{-1}, and the broadening is described as ‘homogeneous’. Under homogeneous broadening conditions, $\Delta^2\tau_c \ll \Delta$, so FHWM(homogeneous) $\ll$ FWHM(inhomogeneous). Of course intermediate rates present difficulties, and, in particular, as the temperature of a system is changed, inhomogeneous broadening can convert to homogeneous, and vice versa.

There have been innumerable papers discussing this phenomenon, and several experimental techniques, which purport to distinguish between homogeneous and inhomogeneous broadening, have been described. These include ‘hole-burning’ methods, but the most recent, and the most successful, have been the so-called ‘vibrational echo’ experiments, exploited in the IR particularly by Fayer and colleagues [13], and in the Raman by Berg and colleagues [14]. (The significance of these and related experiments are discussed in [9].) The general conclusion is that, *usually*, vibrational bands of molecules at r.t., in solvents which are not too viscous, are homogeneously broadened. In all that follows, in both ground state and excited state, we shall assume the vibrational bands to be homogeneously broadened, although as we shall see in Section 4 it is probably irrelevant.

2.4. Dephasing

Assuming that a homogeneous band is Lorentzian, then, as we mentioned earlier, the FWHM is $1/\pi T_2$ Hz. We now need to address the meaning of, and contributions to, T_2. T_2 is called the 'dephasing' time, for reasons that are rather subtle [9], and need not concern us here. Assuming that each contribution to the bandwidth (Γ) has an exponential decay, the relationship is:

$$\Gamma = 1/\pi T_2 = 1/2\pi T_1 + 1/\pi T_2^* + \Gamma_{\mathrm{or}}$$

(Strictly speaking, we also assume a Markovian process, in which the probabilities of any events in a system depend on the state of the system at that time, and not on its previous history. For other dephasing mechanisms see, for example, [15] and references therein).

In this relationship T_1 is the 'vibrational relaxation time', i.e. the time for the molecule to decay from $v = 1$ to $v = 0$; T_2^* is the 'pure dephasing time'; Γ_{or} is the contribution to bandwidth from 'orientational' effects.

For 'largish' molecules, such as coordination compounds in solution at r.t., the contribution from orientational effects is small. Moreover, as pointed out by Hamaguchi [16], for such molecules, promotion to an excited state is only likely to lead to trivial changes in overall geometry, and hence the contribution from orientation to band width in ground and excited states will be the same. Since we are concerned in this review with changes in bandwidth between these states, we shall ignore any orientational contribution.

The vibrational relaxation time, T_1, is best measured directly by either 'one-colour' or 'two-colour' experiments using IR pulsed lasers. For transition metal carbonyls in r.t. solvents, T_1 varies from ~ 10 to ~ 500 ps [17], making a contribution of ~ 0.5–0.01 cm^{-1} to the bandwidth. This is usually a very modest contribution compared with the pure dephasing contribution. We have no reason to assume that T_1 in an electronically excited state will be very different from the ground state—and anyway, as far as the present author is aware, no measurements have been made—so it is again reasonable to assume that T_1 makes only a small contribution to changes in excited state bandwidths.

This leaves 'pure dephasing', with time T_2^*. At the simplest level, T_2^* is a measure of the rapid modulation of the interaction of the vibrational energy levels of a transition (of the solute) with the thermalised bath of the solvent molecules. There have been many attempts to calculate these effects, which in practice involve calculating the appropriate correlation function based on some model of the solute–solvent interaction. FT of the correlation function then gives the spectrum. Predictions are made about the change in pure dephasing with, for instance, viscosity or temperature. It is interesting that the latest IR echo measurements, which provide comprehensive measurements about *all* the contributions to bandwidth, cast doubt on many of the models on which calculations have been based.

This interaction has been described as 'direct' [18], but there is another method of dephasing, described as 'indirect' [18], which is outlined in Appendix A. (There is another dephasing mechanism which involves resonance coupling between identical molecules; however, since we are only considering molecules in fairly dilute solutions, this can be ignored).

2.5. Organic radicals

It is worth mentioning here the work on two organic radicals by Terazima and Hamaguchi [19]. In examining the resonance Raman spectra of the benzosemiquinone radical and the pyrazinyl radical, in 2-propanol solution, the authors noted that the bandwidths were 2–3 times larger than the parent molecules. Since the bands were reasonably well fitted as Lorentzians, it was assumed that the bands were homogeneous, and that the change in bandwidth was due to the change in pure dephasing. If it is assumed that the most likely dephasing mechanism is direct, then, as described above, FWHM $= \Delta^2 \tau_c$. Thus the bandwidth changes because the interaction between radical and solvent is greater than between parent and solvent. This is due either to the increase in the frequency fluctuation (i.e. Δ) or in the correlation time (τ_c), or in both. The authors conclude that change in τ_c is probably the more important, but in any case the change in bandwidth is a direct measure of the change in interaction between molecule–solvent and radical–solvent.

2.6. Vibrational spectra of metal carbonyls

Since much of what follows on excited states concerns transition metal carbonyls, it is useful to make some comments here on their ground state spectra.

The application of the energy factored force field, and the local dipole moment approximation, to transition metal carbonyls has had an enormous impact on understanding their structure, both geometric and electronic, and their behaviour [20–25]. Although there has been limited interest in the shapes of C–O bands, a number of authors have discussed the topic [20,26–28]. The recent IR echo measurements by Fayer and colleagues [13] have provided a very valuable insight into what determines C–O band shapes, and this necessitates a refinement of earlier views. This has been briefly discussed [9], and more details will be published elsewhere [29]. We can summarise some conclusions (some of which coincide with those mentioned by Braterman [20]).

i) The ν(CO) IR bands of metal carbonyls in non-viscous solvents—whether polar or non-polar-at r.t., are mostly Lorentzian and homogeneous. As the temperature is lowered, the bands become more inhomogeneous and more Gaussian.
ii) The r.t. bandwidth is *mostly*[1] determined by 'pure dephasing'; in some cases (e.g. t_{1u} of $W(CO)_6$) it is 'direct' and in some cases (e.g. probably $Rh(CO)_2$(acac)$_2$ [30]) it is 'indirect' involving a low frequency mode such as a M–C stretch.
iii) In the same molecule, the bandwidth can vary dramatically from mode to mode. High-symmetry in-phase vibrations are the narrowest; the greater the number of coupled CO groups in such vibrations, the narrower the band.
iv) The bandwidth is very sensitive to solvent: polar solvents can greatly increase the bandwidth; the high-symmetry in-phase vibrations are the least sensitive. Degenerate vibrations can be very sensitive, which *may* be a consequence of loss of degeneracy; however, non-degenerate, out-of-phase modes can also be very sensitive.

All of this indicates that there is an interaction between the C–O vibration and the solvent molecule, which is increased in polar solvents; the net result is a decrease in the dephasing time T_2, which results in an increase in bandwidth. We can risk a little speculation! If we suppose that ν(CO) homogeneous bandwidths are determined by direct dephasing, then, from Kubo:

$$\Gamma = 1/\pi T_2^* = (1/2\pi)(\Delta^2 \tau_c) \quad \text{(in Hz)}$$

where the correlation time refers to the characteristic time of interaction of the vibrational mode with the solvent. If we assume that this time is unlikely to change dramatically from mode to mode, then the bandwidth will be determined by Δ, i.e. by the spread of perturbed frequencies. This might seem obvious, but it must be recalled that it is only the *in*homogeneous width that is determined solely by the spread of perturbed frequencies. In fact, in the light of the above discussion, we might reasonably conclude that in any event it is the spread of perturbed frequencies that determines the width of the observed band.

3. IR bandwidths in the excited states of coordination compounds

As far as the present author is aware there have been no specific studies of the Raman bandwidths of coordination compounds in excited states. Moreover in looking at many spectra I have not been able to uncover any systems in which clear comments about bandwidths are made, nor where published spectra provide clear data. One of the objects of this review is to encourage such measurements to be made. We have to turn to work on organic systems, of which the S_1 state of *trans*-stilbene has been the most actively studied [1–6]. Although such measurements are really outside the scope of this article, there are some important conclusions which are relevant to this article, and we shall return to a discussion in Section 4. For the moment, we restrict ourselves to the excited state *infrared* spectra of coordination compounds.

3.1. Some preliminary observations

In 1989 Glyn et al. [32] obtained the first IR spectrum of the excited state (MLCT) of a coordination compound, [ClRe(CO)$_3$(4,4′-bipyridyl)$_2$], dissolved in CH_2Cl_2 at r.t. Since the lifetime of the MLCT state is ~1 μs at r.t., this experiment required fast time-resolved infrared (TRIR) spectroscopy. Later work [33] refined the observation and showed that all three ν(CO) bands in the ground state are shifted up in frequency in the excited state; this is because in the MLCT state, the movement of charge to the organic ligand results in partial oxidation of the metal, hence leading to less electron density being available for donation into the π anti-bonding orbitals on the CO groups. Since then, there has been an explosion of interest in the application of TRIR to the interpretation of the electronic properties of the excited states of coordination compounds [34–37], mostly employing C–O and C–N vibrations, but, occasionally, other ligand vibrations. Much of this work has depended on the increasing sophistication of TRIR apparatus, particularly the development of rapid step-scan FT techniques, and the ability to record better quality spectra on shorter time scales.

Returning to [ClRe(CO)$_3$(4,4′-bipyridyl)$_2$]; in addition to the increase in frequency in going from ground to MLCT excited state, there was also an increase in the ν(CO) bandwidths, particularly noticeable in the high frequency a′ band. A similar effect [38,8] is observed for [ClRe(CO)$_3$(bpy)] (bpy = 2,2′-bipyridyl); see Fig. 1. The question is, why? If we ignore rotational effects and assume that T_1 is not too short, the most likely explanation is that the pure dephasing interaction between the excited state and the solvent is stronger than that between the ground state and the solvent. In other words T_2* is shorter in the excited state than in the

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[1] There is evidence [28] that the bandwidth of the Raman-active ν(CO) e_g mode of $M(CO)_6$ (M = Cr, Mo, W) in *n*-hexane has ca. half-and-half rotational and pure dephasing contributions. In other solvents, the contribution from rotation is less. It should also be recalled that for spherical-top molecules, any rotational broadening is expected to be three times larger for Raman bands than for IR bands [31]. Thus the assumption that the IR bandwidth is mostly due to pure dephasing seems reasonable.

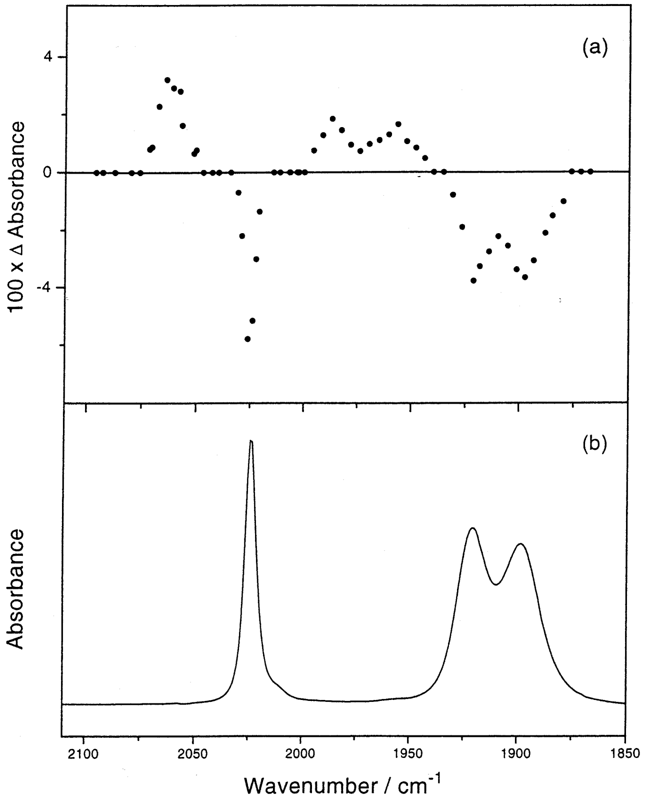

Fig. 1. (a) Time-resolved (TRIR) spectrum, recorded with a diode laser system ~ 50 ns after 308 nm photolysis, of [ClRe(CO)$_3$(bpy)] in CH$_2$Cl$_2$. (b) FTIR spectrum of [ClRe(CO)$_3$(bpy)] in CH$_2$Cl$_2$. The TRIR spectrum shows loss of parent (negative) and generation of three (positive) bands of the lowest MLCT excited state. Reproduced with permission of the American Chemical Society from reference [7].

ground state. If this is correct, then the broadening should depend on the nature of the excited state, and the solvent. Taking the solvent first, and remembering what happens to ground state bands, it is clearly important to examine the behaviour of the excited state bands in different solvents. Unfortunately, because of the kind of compounds studied, the vast majority of published data have been obtained in either CH* is shorter in the excited state than in the ground state. If this is correct, then the broadening should depend on the nature of the excited state, and the solvent. Taking the solvent first, and remembering what happens to ground state bands, it is clearly important to examine the behaviour of the excited state bands in different solvents. Unfortunately, because of the kind of compounds studied, the vast majority of published data have been obtained in either CH$_2$Cl$_2$ or CH$_3$CN. Moreover the afore-mentioned [ClRe(CO)$_3$(bpy)] is not soluble in non-polar solvents. For this reason Clark et al. [7] turned to [W(CO)$_5$(4-acetylpyridine)], whose preliminary excited state IR spectrum (in *n*-heptane) had already confirmed the MLCT nature of the lowest excited state [39]. Fig. 2 shows the ground state IR spectrum in *n*-heptane and CH$_2$Cl$_2$. It is immediately clear that, as expected, the weak high frequency band (symmetric, in-phase) is hardly affected by the change in solvent, but that the two low frequency bands are considerably broadened in the polar solvent (Table 1). Figs. 3 and 4 show the excited state TRIR spectra superimposed, by off-setting the spectra, on the FTIR spectra. What is striking is that the high frequency band is hardly broadened in *n*-heptane but is very much broadened in CH$_2$Cl$_2$. There is a similar effect on the two low frequency bands, but here it is less obvious, largely because these two bands are broader to start with (Table 1). The most obvious explanation is that it is the interaction between the charge-separated excited state and the polar solvent that causes the extra broadening. The fact that the mean frequency shift in *n*-heptane is 46 cm^{-1}, but 66 cm^{-1} in CH$_2$Cl$_2$, is some evidence of greater excited state solute–solvent interaction for the more polar solvent. If this is so, then there should be little extra in broadening in *any* solvent if the excited state has no charge separation. The lowest excited state of [Re(dppz)(CO)$_3$(PPh$_3$)]$^+$ (dppz = dipyrido[3,2-a:2′,2′-c]phenazine) is $^3\pi\pi^*$(dppz); in this excited state the three C–O bands are shifted *down* by about 8 cm^{-1}, and “broadened by ~ 2 cm^{-1}”, i.e. by an insignificant amount, *even in CH$_3$CN* [40]. (This is perhaps not surprising in view of the small effect on the ν(CO) frequencies).

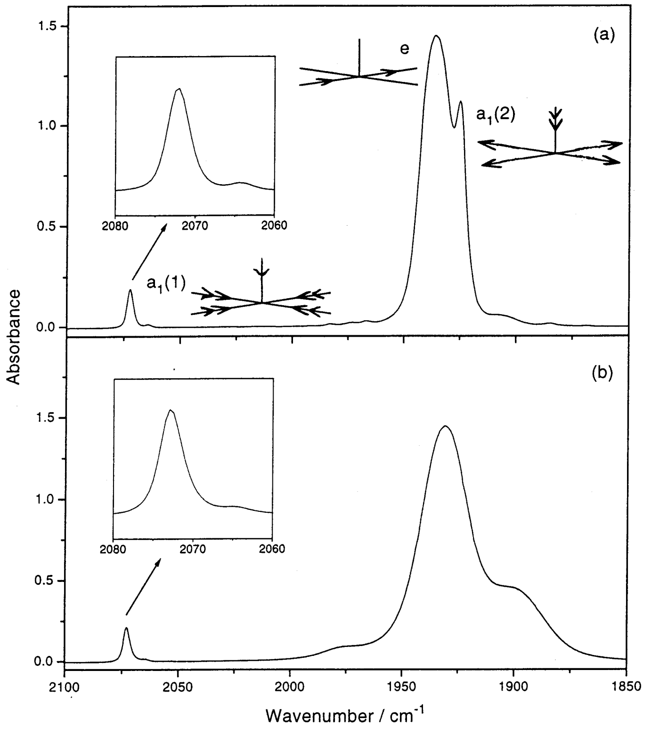

Fig. 2. FTIR spectra of [W(CO)$_5$(4-acetylpyridine)] in (a) *n*-heptane, and (b) CH$_2$Cl$_2$. In both (a) and (b) the insets show the high frequency a$_1$(1) symmetric in-phase band on an enlarged scale. The normal modes are drawn schematically. Reproduced with permission of the American Chemical Society from reference [7].

Table 1
Band positions and bandwidths of the ground (GS) and MLCT excited states (ES) of [W(CO)$_5$(4-acetylpyridine)] in *n*-heptane and CH$_2$Cl$_2$ [7]

Solvent	Mode	Position (cm^{-1}/GS)	FWHM (cm^{-1}/GS)	position (cm^{-1}/ES)	FWHM (cm^{-1}/ES)	Δ(FWHM) (cm^{-1})
n-heptane	$a_1(1)$	2072	3.3	2105	5	1.7
	e	1936	16	2000	19	3
	$a_1(2)$	1924	6	1964	~ 11	~ 5
CH$_2$Cl$_2$	$a_1(1)$	2073	3.6	2114	12	8.4
	e	1931	24	~ 2010	~ 36	~ 12
	$a_1(2)$	1899	28	~ 1976	~ 46	~ 18

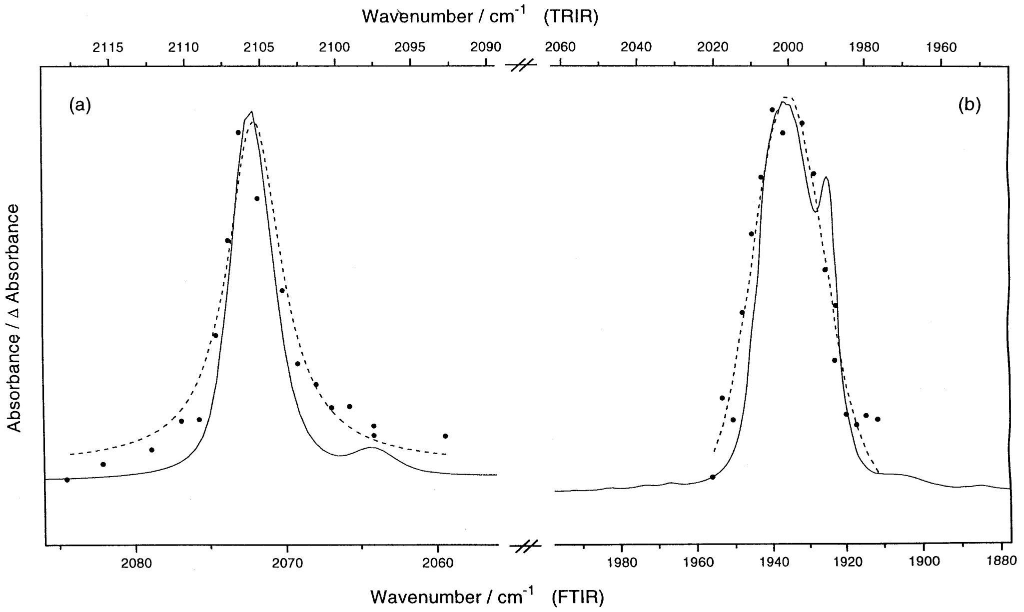

Fig. 3. FTIR (-, lower abscissa) and TRIR (·, upper abscissa, recorded 100 ns after 355 nm photolysis) spectra of [W(CO)$_5$(4-acetylpyridine)] in *n*-heptane: (a) high-frequency $a_1(1)$ band, (b) lower frequency e (FTIR and TRIR) and $a_1(2)$ (FTIR only) bands. For ease of observation, the dotted line represents the best Gaussian fits to the TRIR data. The top and lower abscissa are offset, so that the FTIR and TRIR bands coincide, but are of the same scale. The TRIR spectrum does extend to lower wave number to include the excited state $a_1(2)$ band (which overlaps a band due to the intermediate [W(CO)$_5$·*n*-heptane]).Reproduced with permission of the American Chemical Society from reference [7].

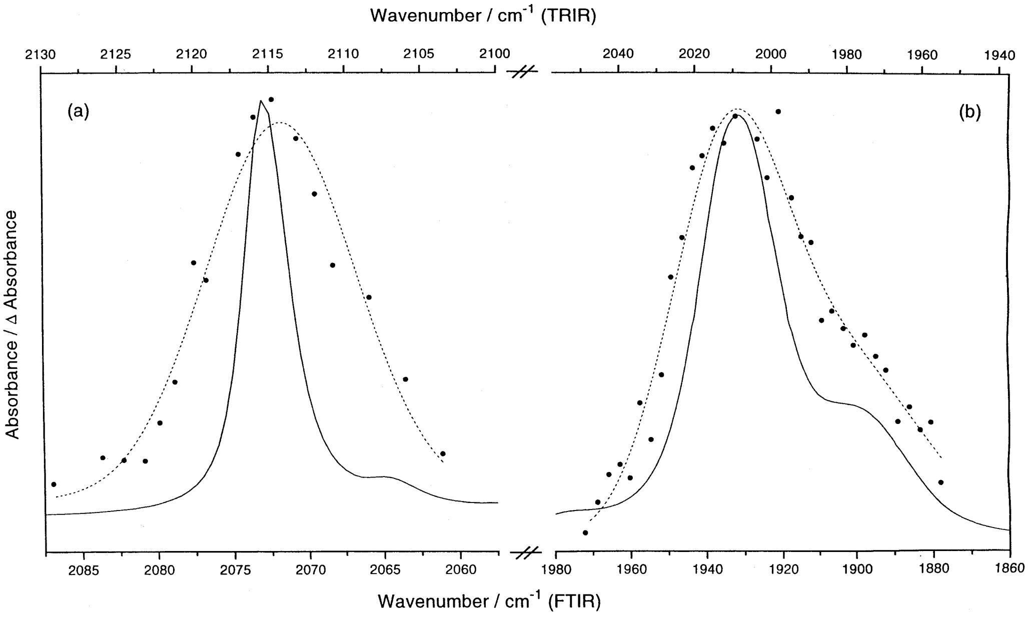

Fig. 4. Similar to Fig. 3, except that the solvent is CH$_2$Cl$_2$. Reproduced with permission of the American Chemical Society from reference [7].

All of the above has made the tacit assumption that, in each case, there is only *one* excited state to be considered. In fact the lowest excited state may involve several close-lying states. For example, for $[ClRe(CO)_3(bpy)]$, careful low-temperature spectroscopic studies show that the lowest emitting MLCT state actually consists of three levels with separation 6.3 and 84.1 cm^{-1} [41]. It is assumed that molecules rapidly exchange between these levels with population determined by the Boltzman distribution. The implication is that the excited state IR is actually probing not one, but three states in rapid equilibrium. How this might affect the spectra we consider later.

3.2. Some further observations

Most of those papers which report TRIR spectra of excited states concentrate on the frequency shifts from ground to excited state. Any change in bandwidth is usually ignored. In the survey that follows, with apologies to the authors where I may have overstepped the mark (!), I have picked out a few interesting examples where the published spectra allow an approximate estimate of what happens to IR bandwidths on promotion to excited states.

3.2.1. ν(CO) bandwidths; 'simple' MLCT states

By 'simple' I mean a transition metal compound with both organic and CO ligands, and in which excitation to the lowest state involves charge transfer to the organic ligand. Perhaps the simplest example is $[Os(CO)(bpy)_2(4,4'\text{-bpy})]^{2+}$, since this compound has a *single* CO group [8,42]. In line with the above discussion of ν(CO) spectra, the single ground state ν(CO) band (1969 cm^{-1}) in CH_3CN solvent is rather broad (FWHM ~ 19 cm^{-1}); on MLCT excitation this band, as expected, shifts up in frequency (2035 cm^{-1}), and also broadens (FWHM ~ 24 cm^{-1}). This is a positive observation, but is not very dramatic, presumably because the ground state band is so broad. A compound with *two* CO groups is $[Re(CO)_2(bpy)\{P(OEt)_3\}_2]^+$ with ν(CO) at 1882 and 1956 cm^{-1}. On MLCT excitation in CH_2Cl_2, the two ν(CO) bands shift up to 1927 and 2012 cm^{-1}, and broaden from FWHM ~ 17 and ~ 14 cm^{-1} to ~ 22 and ~ 23, respectively [43]. Again the effect is positive but not dramatic.

3.2.2. ν(CO) bandwidths; more complex MLCT states

This is best explained by an example. The ground state ν(CO) spectrum of $[(OC)_5W(4,4'\text{-bpy})W(CO)_5]$ in CH_2Cl_2 is essentially that of two overlapping $W(CO)_5$ spectra, similar to that of $W(CO)_5$(4-acetylpyridine) (see Fig. 2). The high frequency band, at 2073 cm^{-1}, is narrow (FWHM ~ 3 cm^{-1}), for the usual reasons (i.e. in-phase symmetric vibration, $a_1(1)$, with five coupled CO groups), and this makes it the most sensitive probe. On excitation, there is charge transfer from *one* W atom to the bridging ligand, and the excited state can be described as the localised structure

$[(OC)_5W^I(L^-)W^0(CO)_5]$ [44]. The band at 2073 cm^{-1} moves in *two* directions, up to 2105 and down to 2059 cm^{-1}; the 2105 cm^{-1} band is the $a_1(1)$ mode of the five COs on the *oxidised* metal, and the 2059 cm^{-1} band is the corresponding mode of the COs on the *unoxidised* metal, the down shift being due to some electron back donation from the charged ligand to the neutral W. The width increases in both cases: from 3 to ~ 13 cm^{-1} for the 2105 band, and from 3 to ~ 15 cm^{-1} for the 2059 band. The effect on 2105 cm^{-1} is in line with the above section. The fact that the 2059 cm^{-1} band is broadened is significant, since it implies that broadening can occur in groups not directly involved in the excited state. (An analogous situation is discussed in Section 3.2.4).

A similar effect [45] is observed for $[(dmb)(CO)_3Re^I(4,4'\text{-bpy})Re^I(CO)_3(dmb)]^{2+}$ (dmb = $4,4'\text{-}(CH_3)_2\text{–bpy}$) in CH_3CN; the excited state is best described as the localised $[(dmb)(CO)_3Re^{II}(4,4'\text{-bpy}^-)Re^I(CO)_3(dmb)]^{2+}$, i.e. with the electron transfer from one metal atom to the bridging ligand. Concentrating again on the high frequency band, this is raised from 2035 to 2074 for the COs attached to Re^{II}, and lowered from 2035 to 2023 for the COs attached to Re^I. However, in this case, although broadening is evident it appears to be less pronounced in the low frequency band.

3.2.3. ν(CO) bandwidths; non MLCT states

In the σπ* excited state of $[Re(benzyl)(CO)_3)(iPr\text{-}DAB)]$ in *n*-heptane, there is very little shift in ν(CO) frequencies from the ground state, and, within experimental error, no change in bandwidths [46].

3.2.4. ν(CN) bandwidths

For $[Rh_2b_4]^{2+}$ (b = 1,3-diisocyanopropane) in CH_3CN [47], excitation from dσ* → pσ gives the $^1A_{2u}$ state, which rapidly inter-system crosses to $^3A_{2u}$. ν(CN) changes from 2193 to 2177cm^{-1} because, in the excited state, there is increased back bonding from metal into the 2pπ* orbital of the C–N group. This produces some charge separation, compared with the ground state, and there is considerable broadening of the C–N stretch in the excited state.

The lowest excited state of $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{II}(bpy)_2\text{-}CN]^+$ in CH_3CN [48] is $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{III}(bpy^-)(bpy)\text{-}CN]^+$, i.e. charge transfer from one Ru to one of its attached bpy ligands. Concentrating on the bridging C–N band, since this is the only clear case, the frequency shifts from 2104 to 2039 cm^{-1}, and broadens very considerably (very approximately 11 cm^{-1} to very approximately 30 cm^{-1}). It is surprising, at first, that the bridging C–N band is shifted to *low* frequency when it is attached to an effectively oxidised metal centre. However, as the authors state "When a good Lewis acid (like Ru(III)) binds to the nitrogen end of a cyanide already bound to a good π-donor centre, π-back bonding to the cyanide is strongly enhanced causing substantial weakening of the C–N bond”. There is thus substantial charge separation. It is interesting to note that on oxidation of $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{II}(bpy)_2\text{-}CN]^+$ to give $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{III}(bpy)_2\text{-}CN]^{2+}$, the bridging C–N vibration shifts from 2104 to 2015 cm^{-1}, presumably for the same reason as above, and shows a bandwidth of very approximately 27 cm^{-1}. This shows, not surprisingly, that band broadening is not a unique feature of electronic excitation, but arises because of the change in charge distribution in the molecule, however, brought about.

Irradiation at 354.7 nm of $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(CN)(bpy)_2]^+$ in CH_3CN [49] causes both $Re^{I} \rightarrow phen$ (~50%) and $Ru^{II} \rightarrow bpy$ (~50%) excitation, but by 200 ns the mixed excited state structure has become solely $[(phen)(CO)_3Re^{I}(NC)Ru^{III}(bpy^-)(bpy)]^+$. Thus the C–O bands are only ~5 cm^{-1} shifted up in frequency, and the $\nu(CO)$ bandwidths appear very similar in ground and excited states. The terminal $\nu(CN)$ band shifts from 2078 to 2135 cm^{-1}, but it is difficult to observe any bandwidth change (The bridging C–N band is not observed in the excited state, and the authors state “it may overlap the terminal $\nu(CN)$ or have a lower oscillator strength”. There is another possibility, which in the light of the observations on $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{II}(bpy)_2\text{-}CN]^+$ [48] seems plausible, and that is that the band has broadened too much to be easily discerned.) It should be added here that this study [49] also included picosecond TRIR, which provided evidence for the initial mixed MLCT state. However, it is important not to interpret bandwidths on short timescales in terms of interaction with solvent. Vibrational lifetimes (T_1) of metal carbonyls can last many picoseconds; because of anharmonicity this means that the $\nu(CO)$ bands are made up of the overlapping spectra of molecules in $v = 1,2,3\ldots$ [17,50]. It is only when vibrational relaxation is complete that the band shape can be analysed in the manner described in this article.

3.2.5. Other modes

An important experiment has been carried out on the excited state of $[Ru^{II}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy)]^{2+}$ in CH_3CN [51]. This complex contains neither conventional metal C–O nor metal C–N stretching vibrations, and the TRIR observations were conducted on the C–O stretching vibration of the ester group. On excitation, this band shifts from 1731 to 1685 cm^{-1}. Together with evidence from other complexes, this shows that “the excited electron is localised on the ester-bearing ligand and that the ester group is highly mixed into the lowest π* acceptor level”; i.e. that the MLCT excited state is mostly $[Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^-)]^{2+}$. The published spectra indicate substantial excited state band broadening, consistent again with the charge separation. The authors also investigated the reaction of the excited state with reductants and oxidants to give, respectively, $[Ru^{II}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^-)]^+$ ($\nu(CO) = 1660$ cm^{-1}) and $[Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy)]^{3+}$ ($\nu(CO) = 1741$ cm^{-1}). Satisfyingly, the 1660 cm^{-1} band is very broad, but the 1741 cm^{-1}band, band, which is only marginally shifted from the parent ground state band, appears little different in width from this band. Similar results have been obtained for other ester substituted ligands [52].

Finally, Schoonover and colleagues [53,54] have managed to obtain the TRIR spectra, in the mid-IR region, of the MLCT excited states of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$. These results confirm earlier resonance Raman data, which were interpreted in terms of a localised excited state model (i.e. $[Ru^{III}(bpy)_2(bpy^-)]^{2+}$ and $[Ru^{III}(phen)_2(phen^-)]^{2+}$), but there was no information provided about bandwidths.

4. Conclusions

Some rather general principles emerge from the observation of IR bandwidth behaviour on electronic excitation of coordination compounds. The first point to make is that nothing seems to contradict the conclusion reached from the experiments on $[ClRe(CO)_3(bpy)]$ [38,8] and, more significantly, $[W(CO)_5(4\text{-}acetylpyridine)]$ [7]. If the lowest excited state involves a degree of charge separation, then, in a polar solvent, there will be broadening of the IR bands when compared with the ground state. In a non-polar solvent, there is no broadening. If the excitation does not involve charge separation, then, usually, the IR bands will be little shifted in frequency from the ground state, and the bandwidth will be hardly affected.

However, these conclusions assume that, in each case, the excited state is single, but, as pointed out in Section 3.1, many of these states are multiple. How might this affect the argument? Consider $[ClRe(CO)_3(bpy)]$, with its three closely spaced levels, as an example. If the C–O bands in each level are very similar, then there will be no observable effect. If the IR(CO) spectra of the three levels are different, then one of two things will happen: (i) if the exchange of molecules between the levels is ‘slow’ then the observed spectrum will be the superposition of the three spectra—in effect an ‘inhomogeneous’ broadening; (ii) if the exchange is ‘very fast’ then some spectral averaging will occur with an effect equivalent to those observed in NMR chemical exchange (For a full discussion of exchange effects on IR spectra see [9]). It is possible that either of these effects is occurring in some of the examples described. How can one evaluate the effects? The short answer is that there is not enough information on excited states to provide an answer. However, one argument suggests that this cannot be the general explanation of bandwidth broadening in excited states: one would not expect change in solvent to have a major effect on the spectra. Because the vast majority of excited state IR spectra have been obtained in the polar solvents CH_2Cl_2 and CH_3CN, most spectra show rather broad ground state bands, so that changes in bandwidth on excitation can be modest. There is a need to examine the behaviour of more compounds in non-polar solvents. Thus we are left with the *tentative* conclusion that treating the IR spectra as arising from one level is probably an acceptable assumption.

Returning to the main theme, this is similar to the conclusions reached by Weaver et al. [55] in their Raman study of the S_1 excited state of *trans*-stilbene. The phenyl C=C stretch in the excited state occurs at 1528 cm^{-1} in *n*-hexane and at 1544 cm^{-1} in CH_3CN, and has a bandwidth of 33 and 43 cm^{-1}, respectively. The difference in shift and bandwidth is attributed, in the case of CH_3CN, to the greater interaction between solvent and the charge separated excited state, which is stabilised by the polar solvent. (It should be noted that we are here considering only the 'static' spectrum which is achieved after several picoseconds, during which time the excited molecule is 'cooling down'. The 'dynamic' behaviour has been the subject of numerous papers [3–6]).

A model which attempts to put this interaction on a quantitative basis has been introduced by Hamaguchi [16]. Since it seems possible, in principle, to extend it to ν(CO) and ν(CN) vibrations of coordination compounds in ground and excited states, it is described in outline in Appendix B.

The band shape and the associated bandwidth of an IR band are a subtle result of the interplay of several factors. In the extreme of inhomogeneous broadening, the band is likely to be Gaussian with a bandwidth $\sim\Delta/2\pi$ Hz; in the homogeneous extreme, it is likely to be Lorentzian with bandwidth $\Delta^2\tau_c/2\pi$ Hz. (Section 2.3) We make the reasonable assumption that we can ignore contributions to the band broadening from vibrational relaxation (T_1) and rotation. Furthermore there seems no reason to assume that the correlation time (τ_c) for a particular mode will change dramatically if the molecule is in an excited state. Thus we conclude that the most important contribution to any change in bandwidth is Δ, whether the band is largely homogeneous or largely inhomogeneous. Why should Δ, the spread in frequencies caused by interaction with the solvent, change from ground to excited state? In the ground state the instantaneous solvent arrangement around a molecule interacts with the vibrational energy levels of the molecule. When the solvent arrangement changes, the interaction changes, and the vibrational levels are altered, producing a frequency shift, hence giving rise to the spread of frequencies, Δ. This interaction clearly depends on the nature of the vibrational mode. [It is worth emphasising that for ν(CO) vibrations, because the signs of the EFFF (energy factored force field) interaction force constants are positive, the band with the narrowest bandwidth is invariably the mode associated with the highest symmetry in-phase vibration. If this mode involves several CO groups coupled together, then, perhaps because it is the most 'shielded' from the solvent, the breadth of the band in the ground state is little affected by change in solvent]. If the excited state produces charge separation then in a polar solvent the interaction energy will be large, and will change more as the instantaneous solvent arrangement changes.

Acknowledgements

It is a pleasure to acknowledge many interesting discussions with Dr Mike George.

Appendix A: 'Indirect' dephasing

In this case, dephasing occurs because of energy exchange between the vibrational mode of interest and, often, a low frequency mode, usually but not necessarily, in the same molecule. Suppose the frequency of the high frequency mode (A) is ω_A when the molecule's low frequency mode (B) is in $v_B = 0$. Due to anharmonicity, when mode B is in $v_B = 1$, the frequency of mode A will be, say, $(\omega_A + \delta\omega)$, where $\delta\omega$ can, of course, be either positive or negative. If the two frequencies of mode A (ω_A and $\omega_A + \delta\omega$) are well separated, and if ω_B is small compared with kT, and if the rate of transition between $v_B = 0$ and $v_B = 1$ is 'slow' then we shall see the main band at ω_A and the 'hot' band at $(\omega_A + \delta\omega)$. What happens if the mode B level interconversion becomes 'fast'? Now we are much more likely to see a single high frequency band. Depending on some assumptions, the effect can be calculated [56]. The *position* of the fundamental, ω is $(\omega_A + \delta\omega_A)$, where its shift, $\delta\omega_A$ is given by:

$$\delta\omega_A = \frac{\delta\omega e^{-(E_B/kT)}}{1 + (\delta\omega)^2\tau^2}$$

The *shape* of the band is given by:

$$I(\omega) = \frac{I(\omega'_A)}{1 + (\omega - \omega'_A)^2 T'^2_2}$$

where:

$$\frac{1}{T'_2} = \frac{1}{T_2} + \frac{(\delta\omega)^2\tau e^{-(E_B/kT)}}{1 + (\delta\omega)^2\tau^2}$$

in which T_2 is the contribution to the dephasing of the band from other sources (e.g. 'direct') in the absence of the A/B energy exchange. Mode A is now a Lorentzian with FWHM equal to $2/T_2'$ rad s^{-1} ($=1/\pi T_2'$ Hz). It should be noted that such a dephasing will be dependent on temperature.

Appendix B: Dynamic polarisation

It is assumed [16] that the C=C group can be highly polarised by interaction with the solvent to give, in the extreme, $C^+–C^-$. In the simplest model it is assumed that the C–C stretching frequency hops between the two values associated with C=C and with $C^+–C^-$. The shape of the resulting single band can be calculated in a manner analogous to that given in Appendix A. The bandwidth depends on the forward and backward hopping rates and on the frequency difference between C=C and $C^+–C^-$. It is then possible to model ca. the real situation in which there is a range of frequencies between C=C and $C^+–C^-$, symbolised by $C^{\delta+}–C^{\delta-}$. Thus the model is a measure of the time-dependent interaction between a highly polarisable molecule and the solvent, i.e. dynamic polarisation.

Since there is nothing unique to the excited state in this model, Hayashi and Hamaguchi [57] have recently employed the methodology to the ground state ν(CO) IR spectrum of acetone. It is supposed that the effect of dynamic polarisation can be expressed as:

$$\omega(t) = \omega_0 + \Delta\omega_{CL}(t) + \Delta\omega_{LJ}(t)$$

(i.e. an extension of the Kubo expression)

where $\Delta\omega_{CL}$ and $\Delta\omega_{LJ}$ are the instantaneous frequency shifts induced by solvents via the long-range Coulomb interactions and the short-range Lennard–Jones interactions, respectively. Via a new way of considering these terms, and applying a molecular dynamics simulation, a band shape for the C=O stretch is obtained. This is very close to the experimental spectrum, which is Lorentzian, implying fast modulation and homogeneous broadening.

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