For: Review in J. Phys. Chem.

The Infrared Dynamics of Iron Diene Complexes*

James J. Turner[+] and Michael Bühl[++]

[+] School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

[++] School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK

*Dedicated to the memory of Friedrich-Wilhelm Grevels, 28.12.1939 – 20.6.2016

Supporting Information

ABSTRACT: The temperature-dependence of the low frequency C-O bands in the IR spectrum of $[(\eta^4\text{-norbornadiene})Fe(CO)_3]$, reminiscent of signal coalescence in dynamic NMR, was interpreted by Grevels (in 1987) as chemical exchange due to very fast rotation of the diene group. Since then there has been both support and objection to this interpretation. In this Review we discuss these various claims involving both one- and two-dimensional IR and, largely on the basis of new DFT calculations, furnish support for Grevels's original interpretation.

1. INTRODUCTION

The compounds (norbornadiene)$Fe(CO)_3$, [NBD] and (butadiene)$Fe(CO)_3$, [BUT] have structures shown in Figure 1. The symmetry of both molecules is C_s and they should show three IR bands in the C-O stretching region, two a' and one a". At room temperature in hydrocarbon solvents, this is precisely what is observed for BUT; Figure 2 shows the original spectrum obtained by Grevels and colleagues[1], with the two low frequency bands assigned as a" (1980 cm^{-1}) and a' (1991 cm^{-1}). However the two low frequency bands of the NBD complex are merged into one broad band at ~ 1970 cm^{-1} (Figure 2).
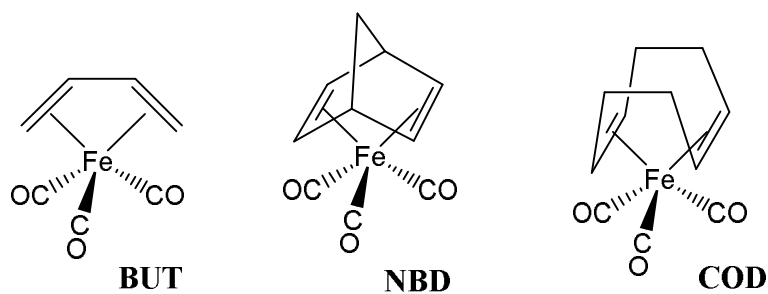
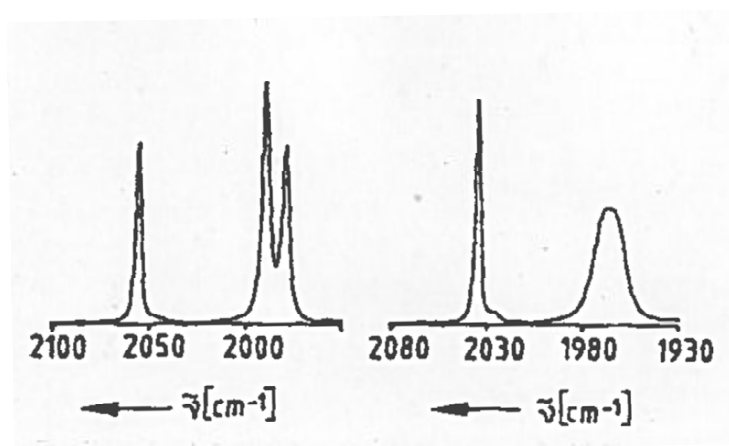**Figure 1**: The (diene)Fe(CO)$_3$ complexes of this study.

Figure 2: The C-O IR bands of (butadiene)Fe(CO)$_3$ [BUT] left, and (norbornadiene)Fe(CO)$_3$ [NBD] (right) in isooctane at 20° C. (Adapted from Figure 1 in ref. 1, reprinted with permission from Wiley-VCH)

It was noted by Grevels and colleagues[1] that the low frequency broad band of NBD in isooctane splits into two on lowering the temperature from room temperature to -80°C (Figure 3). Meanwhile on raising the temperature to 80°C the band narrows (17.5 cm^{-1} at 20°C to 15 cm^{-1} at 80°C).
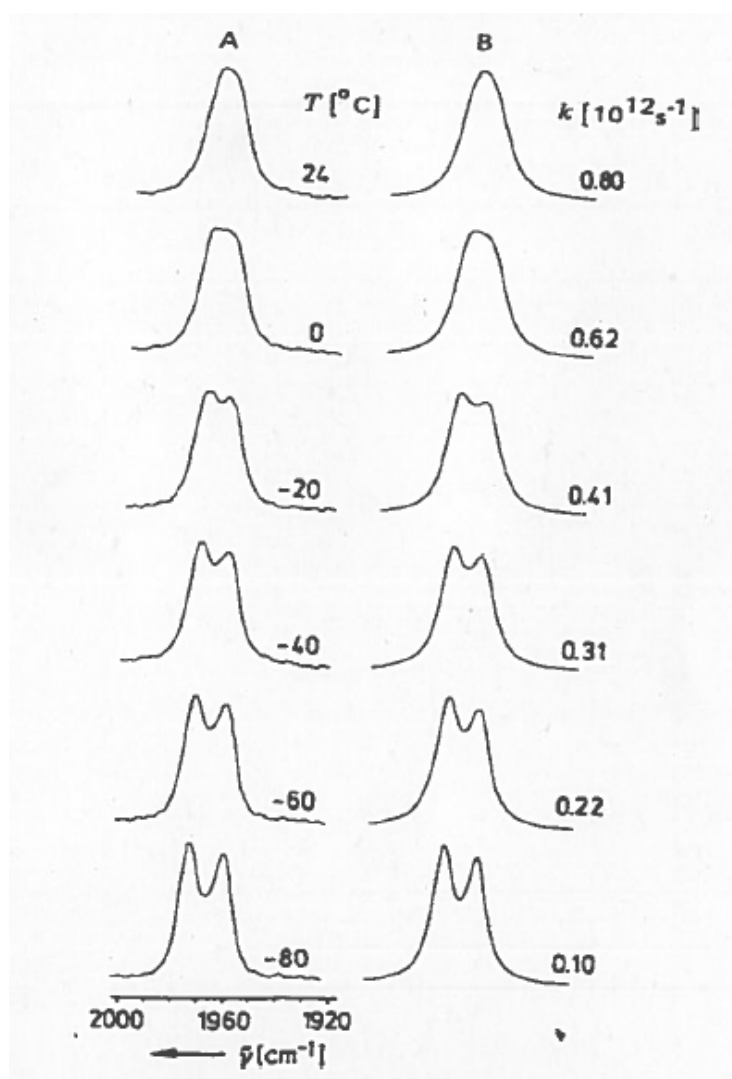
Figure 3: Temperature-dependence of the C-O low frequency IR bands of NBD in isooctane: (A) experimental; (B) simulated. (Taken from Figure 3 in ref. 1, reprinted with permission of Wiley-VCH)

In a later paper[2] in collaboration with one of us, using liquid noble gases as solvents, this is shown more clearly (Figure 4).
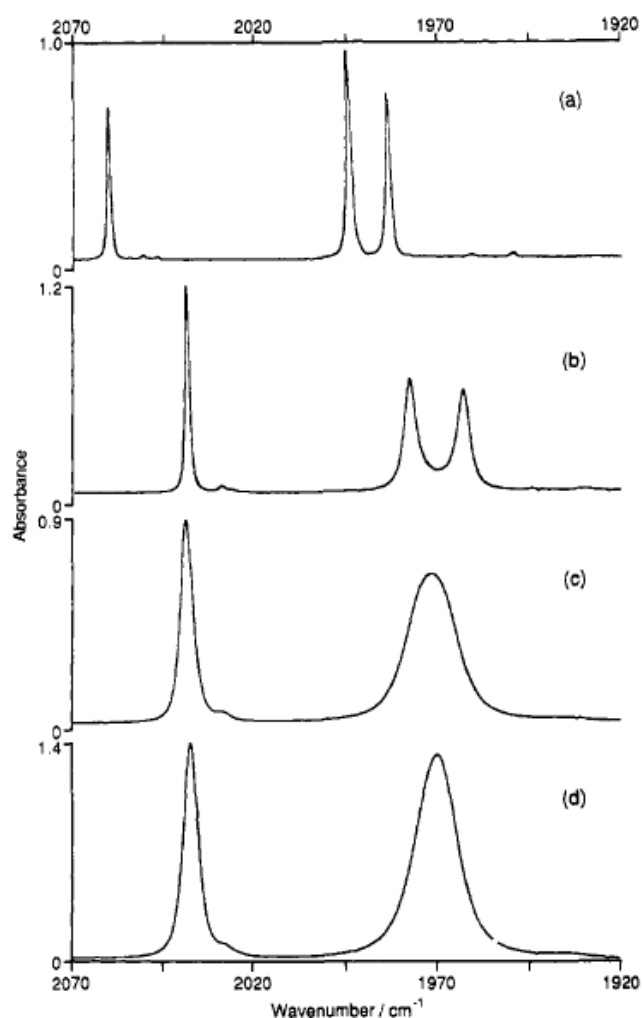
Figure 4: IR spectra in the v(C0) region of (a) BUT in a liquid mixed solution of Kr and Xe (LKr/Xe) at -150 °C, (b) NBD in LKr/Xe at -150 °C (the weak bands in these spectra are due to [13]CO groups in natural abundance), (c) NBD in supercritical Xe at 25.5 OC, and (d) NBD in supercritical Xe at 102 °C (Figure 2 in reference 2, reproduced with permission by the American Chemical Society). (Note particularly the narrowing of the low frequency band in supercritical Xe as the temperature is raised, mimicking NMR behaviour).

On the other hand, in related experiments[1,2], the C-O spectrum of BUT shows essentially no change with temperature. The assumption was made[1] that at the higher temperature the CO groups of NBD are undergoing a very fast "turnstile" motion so that on the IR timescale the CO groups are equivalent with effective symmetry C_{3v} and hence there are only two bands, the high frequency a_1 band at 2038 cm^{-1}, and the low frequency e band at 1970 cm^{-1}.

As the temperature is lowered, the twist slows and the effective symmetry becomes C_s with three IR bands, the higher band being unaffected - with symmetry a' - but the low frequency band splits into two with symmetry a" (1962 cm^{-1}) and a' (1976 cm^{-1}) (Figure 3).Thus the behaviour is reminiscent of NMR band collapse followed by coalescence, but on a much faster timescale. NMR peak separation can be up to hundreds of Hertz, which requires exchange rates of $10^3 - 10^4$ s^{-1} to observe coalescence. In the vibrational case two bands separated by, say 5 cm^{-1} requires an *ultrafast* exchange rate of $> 10^{12}$ s^{-1} to observe coalescence. Thus for BUT, ^{13}C NMR shows exchange[3] on a time scale of the order of 10^4 s^{-1} ,with an activation energy of about 9.5 kcal/mol; i.e. much too slow to show any effects on the IR spectrum.

Using essentially the Bloch methods, Grevels[1] extracted kinetic and energetic information (Figure 3) from the observations on NBD and concluded that the barrier height for the twist in NBD is about 1 kcal mol^{-1}, with a kinetic range of 10^{11} to 10^{12} s^{-1}. He was well aware of possible objections formulated previously by Strauss and coworkers[4] to using the Bloch equations for vibrational spectroscopy but thought his measurements would give an approximate idea of the barrier height. (We return to Strauss's arguments shortly).That is, there is "inter-well" jumping from one potential minimum to another. Similar results to NBD were found for (cyclooctadiene)Fe(CO)$_3$, [COD][1,5] (Figure 1), although this has a different symmetry, and where splitting in the low frequency bands was only observed between -110°C and –120^{0}C (in 2-methylpentane). Grevels pointed out that for BUT, the rotation has to go through 60^0 to reach the transition state, whereas NBD and COD only have to rotate by 30^0; this may be part of the cause of the different activation energies.

Grevels and colleagues followed this up in a series of increasingly sophisticated papers, including collaboration with one of us and colleagues[2] (see Figure 4), employing ^{13}CO substitution and using liquid noble as solvents where the IR bands are particularly narrow. This work culminated in a paper[6] by Grevels, in collaboration with McClung, in which a detailed analysis of precisely how the C-O vibrational modes change on rotation led to a theoretical fit of the band collapse in COD that is so good as to be indistinguishable from the experimental observations.

Others have performed similar experiments. Most notably, in a series of impressive papers, Lear and colleagues have examined some subtle effects on the chemical exchange in the diene complexes. They have shown that Raman spectroscopy mimics the IR data[7], giving activation energies for NBD in 2-methylpentane, of 1.2 +/- 0.2 kcal/mol, and 1.4 +/- 0.1 kcal/mol, from IR and Raman data respectively. The rate constants varied from 1.15 x 10^{12} s^{-1} at 293 K to 0.48 x 10^{12} s^{-1} at 213 K. In other words they get essentially identical results to Grevels'. By choice of a range of solvents, they show that the related compound (η^{4}-cyclooctatetraene)$Fe(CO)_3$, does not show chemical exchange[8]. They also show that the exchange in NBD only slightly changes in a series of linear and non-linear alkanes[9].

On the face of it therefore, it seems that the dynamics of (diene)$Fe(CO)_3$ complexes can be monitored by the simple use of linear (one-dimensional) IR and Raman spectroscopy. However there have been objections to this interpretation, mostly by Strauss, Best and, by implication, Harris. We consider these comments next.

2. DOES DYNAMIC IR MIMIC NMR?

It is useful to look at an energy diagram. Figure 5a is a highly schematic sketch representing two CO groups at different positions (A and B) in a molecule, with different fundamental frequencies, and where the two groups can be linked by rotation between the positions. If the frequencies v_0^A, v_1^A etc are similar then there will be a single IR band at v^A; similarly for v^B. If the barrier to rotation is high, there will be no exchange of CO groups, and the C-O spectrum will consist of two bands. If the barrier is very low, rapid exchange will occur and on the Grevels model there will be merging and coalescing of the bands, mimicking NMR behaviour. What could be wrong with this?
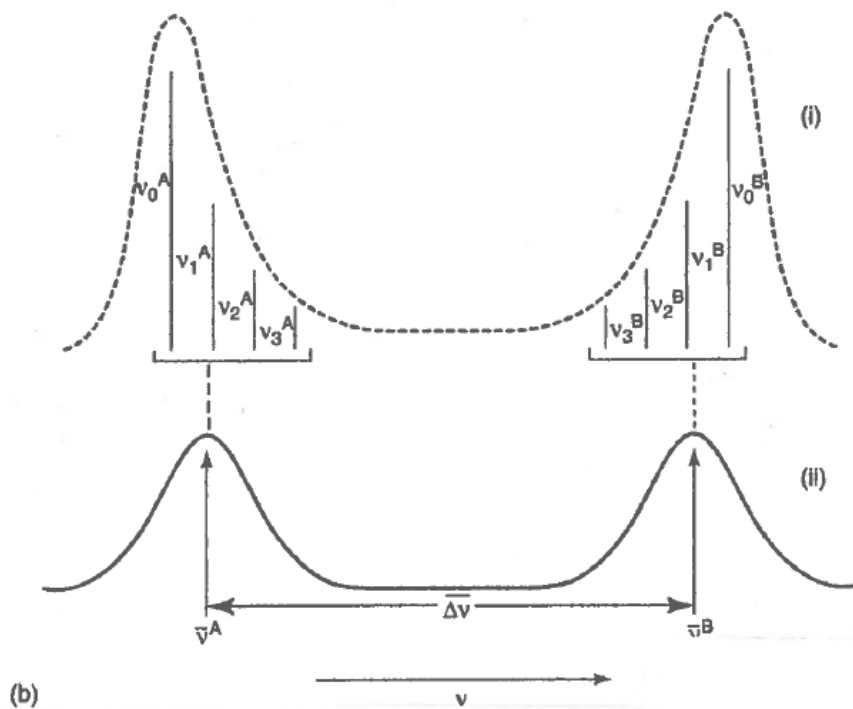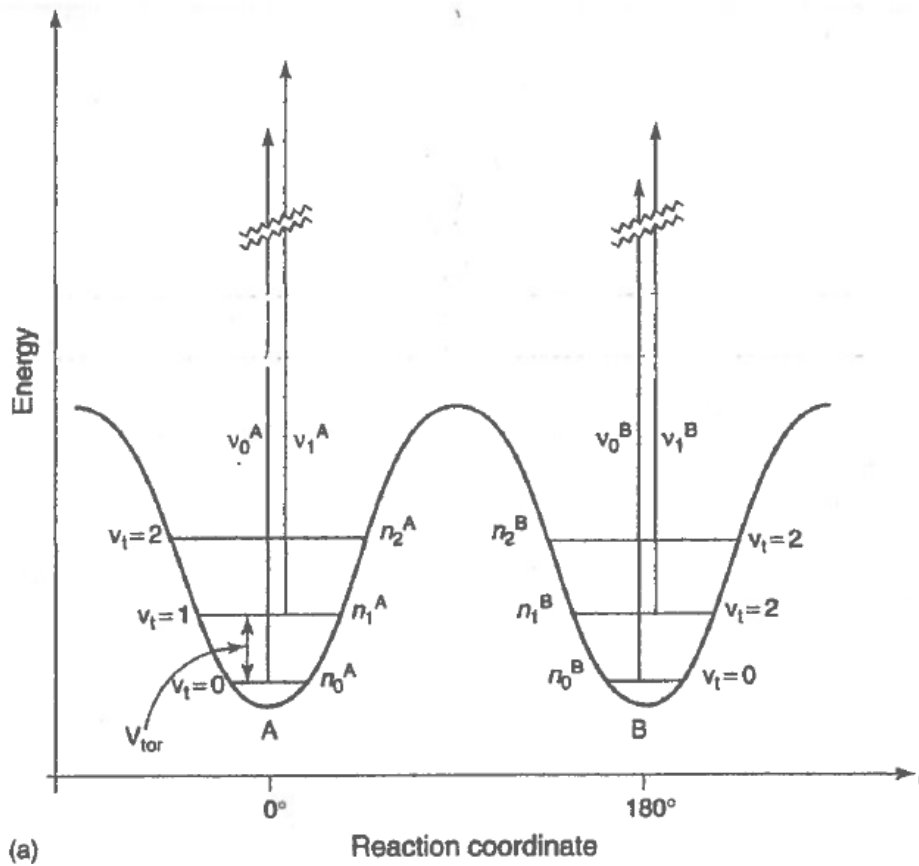
Figure 5: (a) Schematic diagram of the potential function for rotation of two CO groups between positions A and B in a molecule. The torsional levels are denoted by v_t = 1, 2, etc,

and n_m^A represents the population of level m in site A; similarly for site B. v_0^A is the frequency of the C-O stretch in site A from torsional level 0, etc. (b) Schematic representation of spectra to be expected if no exchange is occurring, but vibronic coupling between the torsion and C-O vibrations is large: see text. (Somewhat similar diagrams appear as Figures 11 and 12 in ref. 11). Modified from Figures 3 and 4 in ref 10, with permission from the American Chemical Society.

2.1 The work of Strauss and colleagues

(This is also discussed in the review by one of us[12]). In1985, MacPhail and the late Strauss published an important paper[4]. This was followed by a more developed, much-quoted, review paper[11] in 1990. They objected to the transfer of Bloch equation use from NMR to IR exchange processes. For Bloch equations to be applicable, they state "the transfer between the two sites must be fast enough to cause no change in the phase of the density matrix elements during the transfer". This means that as the group moves from site to site, such as by a rotation, the time taken for this motion (i.e. the transit time) must be very short when compared with the reciprocal of the spread of frequencies which characterize the reaction. In the case of NMR, we can imagine two peaks separated by 10 Hz; the timescale is 1/10 s. With a transit time may of say10^{-12} s, the requirement is satisfied. However if two IR peaks are 10 cm^{-1} apart, the timescale is 3 x 10^{-12} s, which puts it in the range of the transit time. If there is such a rapid process, the rotational barrier must be very low. This means that, in principle, it may be impossible to disentangle the exchange contribution from other contributions to the band broadening. MacPhail and Strauss certainly have a point here, but we believe their conclusions are just too pessimistic.[†]

[†] It is interesting that in an early paper (reference 13), Strauss et al were looking at the IR spectra of the hexadecane-urea clathrate. The doubly degenerate asymmetric C-H stretch shows a single band at room temperature at 2956.6 cm^{-1} with a half-width of ~11 cm^{-1}. However at 9 K, the band splits into two; on raising the temperature the two bands coalesce to the original. They interpreted this as an NMR equivalent collapse, and obtained estimates of the energy barrier. This work came five years before Grevels. However, as is clear from references 4 and 14, the authors changed their minds.

Strauss and colleagues[14] examined the IR temperature behaviour of asymmetric bands of the CH_3 group in a number of higher alkanes. There is evidence for band coalescence. In this case it was proposed that the collapse is caused, not by "inter-well" jumping, i.e .NMR equivalence, but by the change in the C –H vibrations as one climbs the energy levels in the torsional motion, i.e. an "intra-well" mechanism. This is illustrated in Figure 5b(ii); on this assumption, because of vibronic coupling between torsional motion and, in this case, C-H stretches, the frequencies v_0^A, v_1^A, etc are different. If the movement among the torsional levels is very fast then applying Redfield arguments the spectra should show movement together of two Lorentzians, with the degree of coalescence depending on the population of the torsional levels. This may well be the correct explanation for these cases.

In a later paper[15], Strauss applied these arguments to the C-O stretches of NBD. He suggested that for NBD, there is strong vibronic coupling between the torsional twist energy levels (with a torsional frequency of about 23 cm^{-1}) and the C-O vibrations so that the frequency of these vibrations is very sensitive to the twist angle. As the vibrational number of the twist is raised, the low frequency C-O bands shift towards each other, promoting the observation of coalescence without any "inter-well" jumping, i.e. as in Figure 5b(ii).

With some simplifications he *nearly* matches Grevels's observations but with one very important problem (see below). Moreover he suggested DFT calculations would demonstrate the sensitivity of the low frequency bands to twist angle and hence support his mechanism. This DFT calculation was done in collaboration with Thiel by one of us[16]. This shows that the positions of the two low frequency bands hardly change on climbing the torsional well, thus arguing against Strauss's model, and supporting the Grevels model. In the light of Best's conclusions[17] we return to these calculations shortly.

There is a further relevant problem in Strauss's mechanism. As stated above it leads to the broadening and moving together of the two low frequency bands as two Lorentzians. This Redfield mechanism does not lead to any extra build-up of intensity between the bands, an important feature of NMR band collapse[18]; in fact in the early days of NMR, before the advent of dynamic NMR computer programs, approximate estimates of the exchange rate were obtained from the ratio of the intensity in the centre of two collapsing bands to the intensity at the maxima[19]. We showed[10] (Figure 6) that in fact there *is* extra intensity

between the IR bands and hence chemical exchange must be occurring. As expected, in a similar experiment[10], BUT showed no extra intensity between the bands.This extra intensity feature has been emphasised by Lear[9], and is an important point in his attribution of exchange to the behaviour of NBD in a variety of alkane solvents.
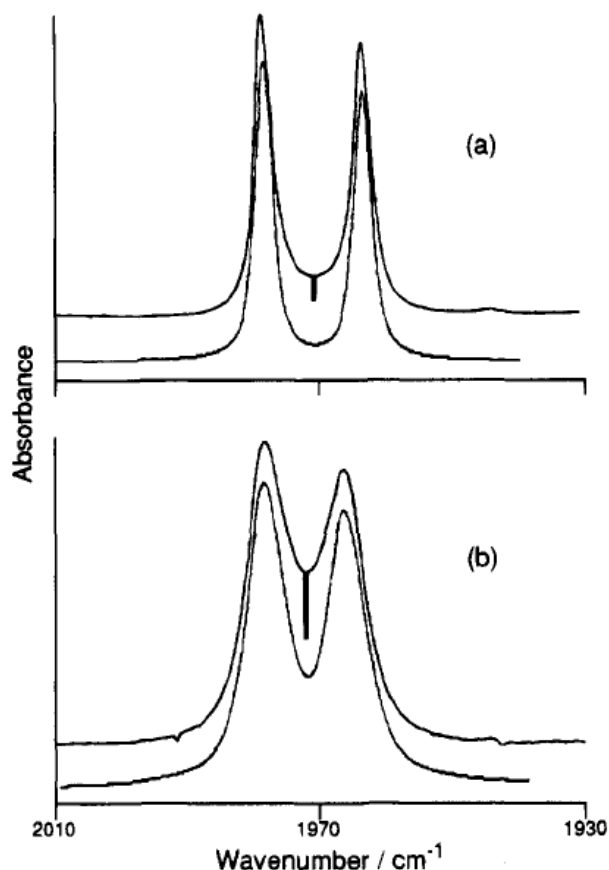

Figure 6: Low frequency pair of C-O IR bands of NBD in liquid Kr/Xe solution at (a) 112 K and (b) 177 K. In both cases the simulated spectra are below the experimental, and are based on the best fit using a Lorentzian/Gaussian program. The thick black lines indicate the extra intensity in the experimental spectra, greater than that predicted on the basis of simple band overlap. Reproduced from Figure 6 in ref. 10 with permission of the American Chemical Society.

Thus by 1995 we believed the inter-well jumping mechanism was secure. This was emphasised by Grevels in the paper referred to above[6]; in an ingenious matrix isolation experiment at very low temperature, the authors were able to demonstrate that

CODFe(CO)$_2$(^{13}CO) with ^{13}CO in the axial position converts to the structure with ^{13}CO in the equatorial position as the temperature is raised from 10 K to 28 K. This proves that there must be a very small barrier to exchange. There the matter rested until the use of two-dimensional IR by Harris and colleagues, which we will consider later. But the important present point is the recent paper by Best et al[17].

2.2 The Work of Best and colleagues

Their paper[17] is mostly concerned with the IR spectroscopic behaviour of ferrocene on interconversion between the D$_{5h}$ and D$_{5d}$ structures, using a technique he calls "Reaction Coordinate Method". As far as we can judge, this seems to be related to Figure 5b(i). Here it is assumed that motion among the torsional levels is slow so that the overall spectrum is a summation of individual $v_m{}^A$ peaks. In order for this to be applicable to NBD, and hence to observe coalescence, he suggests that the DFT calculations of Bühl and Thiel[16], rather than mitigating against the anti-Grevels model, support his interpretation.

In the original DFT calculations[16] on NBD, at the BP86 level with an all-electron polarised split-valence basis (denoted AE1), it was shown, for the ground state, that there is good agreement between theory and experiment, particularly with the important separation between the two low frequency bands of 11 cm^{-1}, compared with experimental value of 14 cm^{-1} (Table 1).

Table 1: CO stretching frequencies (cm^{-1}) in NBD, calculated at the BP86/AE1 level (from reference 14), except where otherwise noted

Structure	a"	a'	a'
Ground state	1971	1982	2026
Ground state (experimental)[a]	*1962*	*1976*	*2038*
Intermediate GS/TS structure [b]	1971	1982	2028
Transition state	1971	1981	2028

[a] From reference 4. [b] Partially optimized structure between ground and transition state.

For the transition state, i.e. at the top of the twist barrier, with a calculated height of 0.6 kcal/mol, the calculated frequency values were virtually indistinguishable from those of the minimum, with essentially the same separation of 10 cm^{-1}. Thus the conclusion was that, contrary to Strauss's suggestion mentioned above, the frequencies of the C-O bands do not vary much with occupation of twist rotational energy levels. This conclusion was greatly reinforced by a DFT calculation of the frequencies at roughly half up the barrier, which showed a low frequency separation of 11 cm^{-1}, i.e. essentially the same as GS and TS (see third entry in Table 1).

Best argues that at the TS, the two low frequency modes swap their character so that the values should be the other way round, ie that 1971 and 1981 should actually be 1981 and 1971, i.e. inverted. Thus, as with Strauss, he concludes that as the twist barrier is climbed the C-O frequencies of the two lower bands move towards each, and eventually cross over (see Figure S1 in the Supporting Information). In this assumption he does not take into account the calculation[16] at half barrier height. If his argument was correct then at this position – or very near it- the two frequencies should be equal as the frequencies cross from GS to TS. In order to check the original DFT calculations, we have now repeated them at the same level, but with more stringent convergence criteria and, instead of arbitrarily fixing a dihedral angle for an intermediate twist structure, we have traced the intrinsic reaction coordinate (IRC)[20,21] connecting ground and transition states. We have subsequently calculated the harmonic frequencies for 7 equidistant points on that IRC path, in which the torsional angle increases in steps of ca. 4^0 (note that this angle is not fixed any more, but optimized in the IRC procedure, see Supporting Material for details). Over the resulting 9 structures (including the stationary points, namely ground and transition state), the three C-O band positions vary between 1971-1971 cm^{-1} (i.e. no change), 1981-1982 cm^{-1}, and 2026-2027 cm^{-1}. Thus the new calculations are virtually identical to the original ones and reinforce the conclusion that there should be no change in band separation with the torsion. This suggests that Best's assumption of the inversion of C-O frequencies is not correct, and hence that his explanation of the coalescence is not valid. The DFT calculations do add further support to the Grevels model.

It is also interesting that Best comments that "the physical interpretation [i.e. of Grevels and Turner] of the calculations is called into question by recent 2D-IR studies[22] of related complexes". We suggest that this does not adequately interpret the 2D-IR and we turn to this topic next.

3. 2D-IR STUDIES ON METAL CARBONYLS

The power of 2D-IR is explained in detail in the book by Hamm and Zanni[23] and in summary in an article by Thielges and colleagues[24]. The relevance of 2D-IR to metal carbonyls has been outlined by Kubarych and colleagues[25]. It is a complex procedure, but for our purposes we can simplify the kind of results by considering a three-level vibrational system (Figure 7).
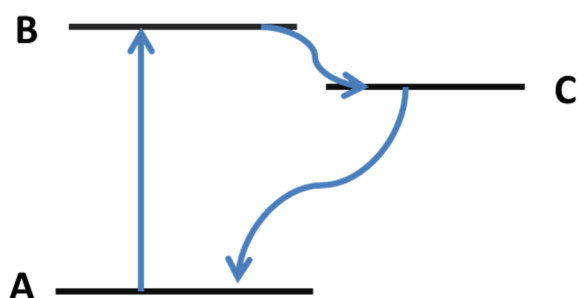

Figure 7: Simple three-level vibrational energy scheme. A is the ground vibrational state, B and C are two excited vibrational states lying close together in energy.

If excitation promotes A $\rightarrow$ B, then as shown, for example, in the elegant work by Heilwell on Rh(CO)$_2$(acac) [26] and W(CO)$_6$ [27] , then using single laser excitation, one can measure several processes, non-radiant transfer B $\rightarrow$ C, and C $\rightarrow$ B (called Intramolecular Vibrational Redistribution, IVR), emission B $\rightarrow$ A and C $\rightarrow$ A, and non-radiative B $\rightarrow$ A and C $\rightarrow$ A We are interested in the non-radiative processes, particularly B $\rightarrow$ C and C $\rightarrow$ A. From the excited levels to the ground state, i.e. direct relaxation, the rate constants can vary significantly, but for metal carbonyls the lifetimes are of the order of 20-100 ps. The IVR rates can also vary, but are usually much faster, with lifetimes 5 -20 ps for metal carbonyls. Thus direct relaxation is unlikely to play a significant part in 2D-IR.

There is of course the complication of chemical exchange which can also induce B → C exchange. Since we are considering exchange rates of the order of a few ps, with 2D-IR there is the problem of disentangling IVR from chemical exchange. Further, how might IVR affect the coalescence measured by conventional FTIR?

Lear[8] makes the point that "steady-state linear spectroscopy is insensitive to contributions from IVR and is only affected by movement along nuclear coordinates". While we essentially agree with this, it is instructive to look a little closer, particularly at Harris's[22] work on the 2D-IR of COD (Figure 1) and BUT, and because of Best's comments[17] about 2D-IR.

3.1 The 2D-IR work by Harris and colleagues

This work uses 2D-IR as a tool to probe the dynamics of metal carbonyl systems, including [22] the coalescing COD and the non-coalescing BUT . In this work the authors appear to underplay Grevels's explanation of band coalescence in COD, although there is some confusion in the paper (see later).

We start with BUT[22]. In this compound the barrier height and relatively slow exchange rate preclude any effects due to exchange in either FTIR or 2D-IR. Thus any observation of effects in 2D-IR must be due to IVR. At 288 K and 198 K, the population loss, which is followed by changes in life-time of the cross peaks, gives IVR lifetimes of 7 +/- 2 and 50 +/- 20 ps respectively. As the authors argue, the variation of IVR rate with temperature should vary approximately exponentially with the separation of the coupling bands. Thus a plot of $\ln(k_{IVR})$ v. 1/T should be linear, which it is. The slope correlates with an activation energy of 1.7 kcal/mol, whereas it is known from NMR studies[3], as mentioned previously, that the activation barrier for exchange is about 9.5 kcal/mol. This confirms what is expected if the population loss rate is due to IVR. In addition, DFT calculations[22] yield an activation energy exchange of 9.3 kcal/mol, satisfyingly in agreement with experiment.

In the original DFT calculations, which Harris and colleagues do not mention, Bühl and Thiel[16] also considered BUT (see Table 2).

Table 2: CO stretching frequencies (cm^{-1}) in BUT, calculated at the BP86/AE1 level (from reference 16), except where otherwise noted.

Structure	a"	a'	a'
Ground state	1985	1995	2044
Ground state (experimental)[a]	*1980*	*1991*	*2056*
Transition state	1981	1983	2032

[a] From reference 1.

A barrier height of 9.4 kcal/mol was computed[16], again in excellent agreement with experiment, and anticipating Harris by 16 years!

The calculated separation of the two low frequency bands in the ground state is 10 cm^{-1} compared with an experimental value of 12 cm^{-1}, reassuringly close. However the separation in the transition state is only 2 cm^{-1}. Depending how far up the torsional barrier one goes, the frequencies should move towards each other, which does not happen in the Grevels experiment. For this reason we have repeated the DFT calculations, again tracing the IRC between minimum and TS and calculating the harmonic vibrations for 6 additional points on the IRC. The results are summarized in Table 3.

Table 3: CO stretching frequencies (cm^{-1}) in BUT, calculated at the BP86/AE1 level along the IRC (value for the coordinate given in amu$^{1/2}$ Bohr, relative energies in kcal mol^{-1}).

IRC	E_{rel}	a"	a'	a'	Δ(a"-a')[a]
Ground state	0.0	1986	1995	2044	9
1.20	0.75	1984	1993	2043	9
1.00	1.86	1982	1992	2041	10
0.80	3.41	1980	1991	2039	11
0.60	5.38	1980	1989	2037	9
0.40	7.45	1980	1986	2035	6
0.20	9.09	1980	1984	2033	4
Transition state	9.70	1981	1982	2032	1

[a] Separation of the two low modes.

The data for the ground state and transition state values are nearly identical with the original calculations. The important point is that the separation of the two low frequency modes hardly changes until one nears the top of the barrier (see last column in Table 3) and so it is not surprising that the FTIR spectrum of BUT shows no change with temperature.

Returning to the 2D-IR work, there is a puzzle. The authors[22] confess that the variation in rate of IVR with temperature is "abnormally strong". An effort is made to comprehend this on the basis of a "wagging" motion, not unlike Strauss's model, but of course with a much higher activation energy. This may be so but we await experiments with shorter time resolution. However the important point to note is that the IVR rate has no effect on the FTIR spectrum.

We now consider COD[22]. Again the rate of population loss is monitored by intensity changes in the cross peaks, giving a linear plot of ln (k) v. 1/T, with lifetimes varying very little on the temperature range 288 K to 198 K, 4.4 +/- 0.7 ps to 7 +/- 2 ps. An activation energy of 0.3 +/- 0.5 kcal/mol is obtained. The authors conclude "This temperature variation agrees well with the weak dependence predicted by an IVR-based mechanism". (This is a little different from the BUT arguments).

They also comment that "all previously published studies of the complex [COD] agree that the barrier to turnstile exchange is ~1.5 kcal/mol. Any contribution from turnstile exchange must be small, on the order of experimental error".

In several places in the paper, Harris et al[22] seem to imply that they are doubtful about Grevels's explanation of coalescence: "the principal source of population transfer in both BUT and COD is IVR"; "the population transfer of COD is also consistent with IVR, not chemical exchange". However, the paper states "Though 2D-IR could not be used to directly observe exchange in COD, the DFT studies performed indicate that the application of the optical Bloch equations to this system results in an accurate measure of the barrier height associated with chemical exchange of the carbonyl ligands".

In order to assess the importance of exchange we have performed DFT calculations on COD (Tables S2 and S3 in the Supplementary Information). Over the two stationary points (GS

and TS) and additional 6 points on the IRC in between, the C-O frequencies varied between 1962 – 1965 cm^{-1}, 1976 - 1977 cm^{-1}, and 2019 – 2021 cm^{-1}. In this case we also repeated the calculations with a bigger basis set denoted ECP2 (with a relativistic pseudopotential on Fe and a diffuse polarized valence-triple zeta basis). This resulted in small changes of the frequencies (now varying between 1941 – 1945 cm^{-1}, 1957 - 1957 cm^{-1}, and 2006 – 2008 cm^{-1}), but importantly the difference between the two lower modes stays the same, always exceeding 11 cm^{-1} (if anything, there is a slight increase in that difference on going from the GS to the TS).

Thus there is no evidence from 2D-IR for the coalescence in COD (and NBD) being due to a Strauss or Best explanation, but that coalescence fits neatly with a Grevels mechanism.

What is the overall conclusion of the 2D-IR work on COD? Simply that it says nothing about chemical exchange observed by conventional FTIR measurements. What is important in FTIR coalescence observations, is to augment them by DFT calculations to eliminate the possibility that frequencies are merging for some other reason than exchange.

3.2 Some other relevant 2D-IR metal carbonyls studies

Some of the most important early experiments on metal carbonyls were carried out by Tokmakoff and colleagues[28] on $Rh(CO)_2(acac)$. In these experiments, they unravelled the subtleties of IVR and coherence. However these studies are less relevant to the problems of chemical exchange.

Harris and colleagues have also performed 2D-IR experiments on $Fe(CO)_5$ [29]. NMR studies with the ^{13}CO enriched compound show that at all temperatures, the exchange between axial and equatorial carbonyl groups is so fast that only one peak is seen[18]. However we did manage to show[30] many years ago that by photolysing $Fe(CO)_5$ in a solid CO matrix at 20 K with polarised light it was possible to maintain oriented $Fe(CO)_5$ molecules indefinitely. The authors[29] suggest that FTIR measurements "show some evidence of coalescence" although compared with Grevels's observations on NBD and COD, the evidence is not very strong.

Moreover it is not possible to heat solutions of $Fe(CO)_5$ high enough to observe coalescence because the molecule decomposes. 2D-IR spectra, collected at three different temperatures, give lifetimes of 8.0 +/- 0.6 ps at 18°C, 6.3 +/- 0.8 ps at 50°C, and 4.6 +/- 0.4 ps at 90°C. An Arrhenius plot gives a straight line with an activation energy of 1.6 +/- 0.3 kcal/mol. This is in reasonable agreement with the DFT calculated barrier height of 2.13 kcal/mol for the Berry pseudo-rotation. It is concluded that this variation supports chemical exchange, partly on the grounds that "Between 18°C and 90°C, we would expect the IVR rate to increase by ~26% (see supporting evidence), yet we observe a change in rate three times greater over this temperature range". Interestingly this argument is not used in the discussion[20] of the 2D-IR on BUT. It is noteworthy that in the supporting evidence it is stated: "These results also imply that the analysis given by Grevels et al. for the line shapes of $Fe(CO)_3(\eta^4$-1,5-cyclooctadiene) is physically sound and could be further confirmed with 2D-IR spectroscopy".

In recent years, Kubarych and colleagues have produced a wealth of 2D-IR experiments on metal carbonyls. We look at those publications most relevant to the present discussion.

Dicobalt octacarbonyl ($Co_2(CO)_8$), has a congested C-O FTIR spectrum, due to overlapping features of the three structural isomers. Kubarych et al[31] emphasise one of the important features of 2D-IR in that it "reveals information hidden in a congested linear spectrum by spreading it over two axes". Employing this argument, they are able to show conclusively that variation in intensity with time of one of the 2D-IR peaks can be assigned to chemical conversion from isomer II to I with a lifetime of 13 +/- 1 ps. This was confirmed by temperature variation studies which gave an activation energy for this conversion of 5.4 kcal/mol. In this important experiment therefore it was possible to distinguish chemical exchange from IVR and obtain detailed kinetic information. It is important to note that the barrier is too high to observe coalescence effects in the FTIR spectrum. In a later paper[32], principally investigating the effect of solvent on the dynamics of $Co_2(CO)_8$, the authors perform DFT calculations on the complex and obtain activation energies for isomer inter-conversion roughly in agreement with the experimental value. Similar experiments[31] were performed on the complexes $[CpFe(CO)_2]_2$ and $[CpRu(CO)_2]_2$. Interestingly, although it was

possible to extract kinetic details, it proved impossible to measure isomeric exchange because of the very low concentration of the relevant isomer.

In a fascinating recent paper[34], Kubarych et al, look at the dynamics of the almost barrierless rotation of benzene chromium tricarbonyl, $(C_6H_6)Cr(CO)_3$, (BCT) in a series of nonpolar linear alkane solvents. Although it is known that bulky side groups can slow the rotation speed down to bring the molecule into the NMR range, BCT itself rotates too fast to yield distinguishable NMR signals. Unfortunately the exchange rate is so fast that even FTIR shows no *splitting* of the IR bands at the lowest temperature available. Detailed calculations however suggest a barrier of 0.28 kcal/mol. Assuming the Bloch equations apply, they predict a slight broadening of the FTIR bands, which is observed.

Woutersen and colleagues[35] conclude from 2D-IR studies that in $Fe(CO)_4$(cinnamic acid) and $Fe(CO)_4$(dimethyl fumarate), cross peak dynamics is determined by IVR, so the complexes exhibit no fluxionality on the picosecond timescale.

For $Mn(CO)_5Br$, Wang and colleagues[36] estimate the barrier for conversion from the C_{4v} ground state to a C_s twisted structure to be >5 kcal/mol. Not surprisingly the effect on the FTIR spectrum is zero. In subtle 2D-IR experiments, using naturally occurring ^{13}C, the authors show that cross peak changes are due to IVR.

There is a particularly significant recent paper by Kubiak, Harris and colleagues[37]. For some time, coalescing FTIR bands in a series of bridged mixed valence dimers of the type $[Ru_3(O)(OAc)_6(CO)L]$-BL-$[Ru_3(O)(OAc)_6(CO)L]$ have been associated with intramolecular electron transfer[38], in the manner of Grevels on the dienes, with time constants ranging from 0.35 ps to ~10 ps. It is now shown, with 2D-IR measurements that no electron site exchange occurs on the time scale required to explain the observed coalescence. The high variability in FTIR peak shapes for these mixed valence systems is suggested to be the result of "fluctuations in the charge distributions at each metal cluster within a single-well potential energy surface". Thus the charge distribution is very sensitive to the torsional twist angle. DFT calculations suggest a barrier height sufficient to limit electron transfer to >160

ps, clearly much too high to have a direct effect on the FTIR spectrum.

4. CONCLUSIONS

Where does this leave us on metal carbonyl IR measurements? Some important messages:

1.   Coalescing FTIR in metal carbonyls nearly always indicates chemical exchange, but beware.

2.   2D-IR measurements are often confusing, and it is frequently impossible – but not always – to extract meaningful data about chemical exchange.

3.   It is ALWAYS important to do DFT calculations to estimate barrier heights and the effect of torsional (or other motion) on the C-O stretching frequencies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ??

Computational details on NBD, BUT and COD, and the IR C-O spectra and calculations by Best and colleagues[17] (S3).

AUTHOR INFORMATION

Corresponding authors

E-mail: james.turner@nottingham.ac.uk

E-mail: mb105@st-andrews.ac.uk

Author contributions

Both authors contributed equally to this Review.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

REFERENCES

(1)   Grevels, F.-W.; Jacke, J.; Klotzbücher, W. E.; Kruger, C.; Seevogel, K.; Tsay, Y.-H. Dynamic Processes on the IR Time Scale: Coalescence of CO Stretching Vibrational Bands in [(η^4-Diene)Fe(CO)$_3$] Complexes. *Ang. Chem., Int. Ed. Eng*. **1987**, 26, 885-887.

(2)   Turner, J. J.; Grevels, F.-W.; Howdle, S. M.; Jacke, J.; Haward, M. T.; Klotzbücher, W. E. Dynamic IR Spectroscopy: Occurrence and Predictability of Coalescence in the CO Vibrations of ^{13}CO-Enriched Tricarbonyl(η^4-norbornadiene)iron. *J. Am. Chem. Soc*. **1991**, 113, 8347-8353.

(3)   Kruczynski, L.; Takats, J. Intramolecular Rearrangement in (η-Diene)tricarbonyliron and -Ruthenium compounds. A Carbon-13 Nuclear Magnetic Resonance Study. *Inorg. Chem.* **1976**, 15, 3140-3147.

(4)   MacPhail, R. A.; Strauss, H. L. Can the Bloch Equations Describe the Vibrational Spectra of a Reacting Molecule? *J. Chem*. *Phys.* **1985,** 82, 1156

(5)   Grevels, F.-W.; Jacke, J.; Seevogel, K. Dynamics of Metal Carbonyls on the Infrared Time Scale: Coalescence of CO Stretching Vibrational Bands. *J. Mol. Struct*. **1988**, 174, 107-112.

(6)   Grevels, F.-W.; Kerpen, K.; Klotzbücher, W. E.; McClung, R. E,. D.; Russell, G.; Viotte, M.; Schaffner, K. The Very Low Barrier of CO Site Exchange in Tricarbonyl(η^4-1,5-cyclooctadiene)iron: Picosecond Kinetics in Solution Investigated by Line Shape Simulation of the (CO) IR Bands and Complementary Evidence from the Course of [13]CO Incorporation in a Low-Temperature Matrix. *J. Am. Chem. Soc*. **1988,** 120, 10423-10433.

(7)   Giordano, A. N.; Morton, S. M.; Jensen, L.; Lear, B. J.; Direct Test of the Equivalency of Dynamic IR and Dynamic Raman Spectroscopies As Techniques for Observing Ultrafast Molecular Dynamics*. J. Phys. Chem. A* **2013,** 117, 2067-2074. He makes a slight alteration to one of Grevels's equations in reference 5.

(8)   Giordano, A. N.; Lear, B. J. Solvent versus Temperature Control over the Infrared Band Shape and Position in $Fe(CO)_3$(η^4-Ligand) Complexes. *J. Phys. Chem. A* **2013,** 117, 12313-12319.

(9)   Giordano, A. N.; Lear, B. J. Comparing the Energetic and Dynamic Contributions of Solvent to Very Low Barrier Isomerization Using Dynamic Steady-State Vibrational Spectroscopy. *J. Phys. Chem. A* **2015**, 119, 3545-3555.

(10)   Turner, J. J.; Gordon, C. M.; Howdle, S. M. Infrared Spectral Features Due to Very Rapid Fluxional Motion: Changes in the Infrared Carbonyl Stretching Spectra of Tricarbonyl(η^4-norbornadiene)iron with Temperature. *J. Phys. Chem*. **1995**, 99, 17532-17538.

(11)   Wood, K. A.; Strauss, H. L. Broadening and Shifts of Vibrational Bands Due to the Effect of Thermal Chemical Reactions. *J. Phys. Chem*. **1990**, 94, 5677-5684.

(12)   Turner, J. J. Bandwidths, in *Handbook of Vibrational Spectroscopy*, eds. Chalmers, J. M.; Griffiths, P. R. John Wiley and Sons Ltd, Chichester, U.K., 2002*.*

(13)   MacPhail, R. A,; Snyder, R. G.; Strauss, H. L. Motional Collapse of Methyl Group Vibrational Bands. *J. Am. Chem. Soc.* **1980**, 102, 3976.

(14)   MacPhail, R. A.; Snyder, R. G.; Strauss, H. L. The Motional Collapse of the Methyl C-H Stretching Vibration Bands. *J. Chem. Phys*. **1982**, 77, 1118-1137.

(15)   Strauss, H. L. Spectra Changes of the Carbonyl Stretching Spectra with Temperature. *J. Am. Chem. Soc*. **1992**, 114, 905-907.

(16)   Bühl, M.; Thiel, W. A Density Functional Study of the Rotational Barrier of Tricarbonyl(η^4-norbornadiene)iron. Effect of the Torsional Angle on the Carbonyl Stretching Spectra. *Inorg. Chem*. **1997**, 36, 2922-2924.

(17)   Best, S. P.; Wang, F.; Islam, M. T.; Islam, S.; Appadoo, D.; Trevorah, R. M.; Chantier, C. T. Reinterpretation of Dynamic Vibrational Spectroscopy to Determine the Molecular Structure and Dynamics of Ferrocene. *Chemistry-A European Journal*. **2016**, 22, 18019-18026.

(18)   Sandstrom, J. *Dynamic NMR Spectroscopy*, Academic Press, London (1982)

(19)   Rogers, M. T.; Woodbrey. A Proton Magnetic Resonance Study of Hindered Internal Rotation in Some N,N-Dimethylamides. *J. Phys. Chem*. **1962**, 66, 546.

(20)   Gonzales, C.; Schlegel, H. B. An Improved Algorithm for Reaction Path Following. *J. Chem. Phys.* **1989**, 90, 2154-2161.

(21)   Gonzales, C.; Schlegel, H. B. Reaction Path Following in Mass-Weighted Internal Coordinates. *J. Phys. Chem.* **1990**, 94, 5523-5527.

(22)   Hill, A. D.; Zoerb, M. C.; Nguyen, S. C.; Lomont, J. P.; Bowring, M. A.; Harris, C. B. Determining Equilibrium Fluctuations Using Temperature- Dependent 2D-IR. *J. Phys. Chem. A* **2013**, 117, 15346-15355.

(23)   Hamm, P.; Zanni, M. *Concepts and Methods of 2D Infrared Spectroscopy*, Cambridge University Press: Cambridge, 2011.

(24)   Le Sueur, A. L., Horness, R. E.; Thielges, M. C. Applications of Two-Dimensional Infrared Spectroscopy. *Analyst*, **2015**, *140*, 4336-4349.

(25)   Baiz, C. R.; McRobbie, P. L.; Anna, J. M.; Geva, E.; Kubarych, K. J. Two-Dimensional Infrared Spectroscopy of Metal Carbonyls. *Acc. Chem. Res.* **2009**, 42, 1395-1404.

(26)   Beckerle, J. D.; Casassa, M. P.; Cavanagh, R. R.; Heilweil, E. J.; Stephenson, J. C. Sub-Picosecond Time-Resolved IR Spectroscopy of the Vibrational Dynamics of $Rh(CO)_2(acac)$. *Chemical Physics*, **1992**, 160, 487-497.

(27)   Arrivo, S. M.; Dougherty, T. P.; Grubbs, W. T.; Heilwell, E. J. Ultrafast Infrared Spectroscopy of Vibrational CO-Stretch-Up-Pumping and Relaxation Dynamics of $W(CO)_6$. *Chem. Phys. Letters*, **1995**, 235, 247-254.

(28)   Khalil, M.; Demiirdoven, N.; Tokmakoff , A. Vibrational Coherence Transfer Charactertized with Fourier-Transform 2D IR Spectroscopy. *J. Chem. Phys*. **2004**, 121, 362-373; and references quoted therein.

(29)   Cahoon, J. F.; Sawyer, K. R.; Schlegel, J. P.; Harris, C. B. Determining Transition-State Geometries in Liquids Using 2D-IR. *Science*, **2008**, 319, 1820-1823.

(30)   Burdett, J. K.; Grzybowski, J. M.; Poliakoff, M.; Turner, J. J. Freezing out the Fluxional Behaviour in Iron Pentacarbonyl and Other Metal Carbonyls. *J. Am. Chem. Soc*. **1976**, 98, 5728-5729.

(31)   Anna, J. M.; Ross, M. R.; Kubarych, K. J. Dissecting Enthalpic and Entropic Barriers to Spectroscopy*. J. Phys. Chem. A* **2009**, 113, 6544-6547.

(32)   Anna, J. M.; Kubarych, K.J. Watching Solvent Friction Impede Ultrafast Barrier Crossings: A Direct Test of Kramers Theory. *J. Chem. Phys.* **2010**, 133, 174506.

(33)   Anna, J.M.; King, J. T.; Kubarych, K. J. Multiple Structures and Dynamics of $[CpRu(CO)_2]_2$ and $[CpFe(CO)_2]_2$ in Solution Revealed with Two-Dimensional Infrared Spectroscopy. *Inorg. Chem*. **2011**, 50, 9273-9283.

(34)   Nilsen, I. A.; Osborne, D. G.; White, A. M.; Anna, J. M.; Kubarych, K. J. Monitoring Equilibrium Reaction Dynamics of a Nearly Barrierless Molecular Rotor Using Ultrafast Vibrational Echoes. *J. Chem. Physics*, **2014,** 141, 134313.

(35)   Panman, M. R.; Newton, A. C.; Vos, J.; van den Bosch, B.; Bocokic, V.; Reek, J. N.H.; Woutersen, S. Ultrafast Dynamics in Iron Tetracarbonyl Olefin Complexes Investigated with Two-Dimensional Vibrational Spectroscopy. *Phys. Chem. Chem. Phys*. **2013**, 115, 1115-1122.

(36)   Yang, F.; Zhao, J.; Wang, J. Two-Dimensional Infrared Study of [13]C- Natural Abundant Vibrational Transition Reveals Intramolecular Vibrational Redistribution Rather than Fluxional Exchange in $Mn(CO)_5Br$. *J. Phys. Chem. B*, **2016**, 120, 1304-1311.

(37)   Zoerb, M. C.; Henderson, J. S.; Glover, S. D.; Lomont, J. P.; Nguyen, S. C.; Hill, A. D.; Kubiak, C. P.; Harris, C. B. Electron Dynamics and IR Peak Coalescence in Bridged Mixed Valence Dimers Studied by Ultrafast 2D-IR Spectroscopy. *J. Phys. Chem. B* **2015**, 119, 10738-10749.

(38)   Londergan, C. H.; Kubiak, C. P. Electron Transfer and Dynamic Infrared-Band Coalescence: It Looks Like Dynamic NMR Spectroscopy, but a Billion Times Faster. *Chemistry-A European Journal*, **2003**, 9, 5962-5969.

Graphical Abstract