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A REPLY TO RECENT COMMENTS {1} ON FAR INFRA RED STRUCTURE
IN LIQUID ACETONITRILE.

by

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ABSTRACT

In a reply to comments by Birch and Yarwood {1} on far infra red peaks in acetonitrile, it is argued that the 10 to 20 % uncertainty in the data obtained by these authors is too high for any conclusion to be drawn, that the purported comparison with the data of G. J. Evans {2-4} is spurious, and that Birch and Yarwood did not refer to a key theoretical paper by Coffey et al. {5} which demonstrates analytically and numerically that far infra red peaks are feasible and are a general feature of the liquid and liquid crystalline states of matter. No reference was made {1} to the key experimental data of G. J. Evans {8}.

INTRODUCTION

Recently, G. J. Evans {2-4} has pioneered far infra-red power absorption spectra of liquid crystals and molecular liquids in which underlying structure was resolved. These spectra were obtained under a variety of conditions and were checked for reproducibility. For example, aliasing was removed with careful use of filters, and the noise level in the power absorption coefficient reduced to about $\pm 1\%$. These prominent features cannot therefore be attributed to simple artifact. Repeated, careful, measurements over a period of some thirty six ~~man~~ months, with several permutations of apparatus, demonstrated reproducibility and repeatability. Shortly after this work appeared, the first complete theoretical explanation of far infra red peaks was produced by Coffey, Corcoran and M. W. Evans {5} using the well accepted itinerant oscillator model {6,7} of the liquid state of matter. The latter was re-worked in terms of normal modes. The analytical theory was tractable when stochastic torques are weak in comparison with their deterministic counterparts, and the analytical theory revealed a peak structure in **liquids** in the far infra red. This structure consistent^d of

several harmonic frequencies for the simplest type of itinerant oscillator, described by eqns (1) and (2) of ref. {5}, in which there occurs only one fundamental frequency. It was found numerically that the peak structure persists even when the stochastic friction is significant {5}, i.e. under conditions normally associated with the liquid state. The results of the calculation were presented {5} essentially in terms of complex dielectric loss, (Figs. (1) and (2) of ref. {5}). Translated into power absorption coefficients, these **theoretically produced** peaks dominate the spectral landscape. By varying the theoretical parameters {5} it was found possible to broaden and sharpen the peak structure and to shift the relative positions of the far infra red resonances and broad, lower frequency, dielectric loss.

The key experimental work of G. J. Evans, and theoretical work of Coffey et al. show that a well resolved structure in the far infra red spectrum of molecular liquids can be reproduced analytically or numerically. By developing the theoretical ideas for use with cosine potentials {6}, or a more realistic representation of intermolecular potentials, it becomes obvious that the far infra red spectrum of liquids is always made up of combination of peak patterns. This conclusion follows straightforwardly from the analytical solution, eqn. (17), of the itinerant oscillator model used by Coffey et al. {5}. A "broad band" in ^{the} ~~the~~ far infra red may be due to insufficient resolution, or to the fact that the overlapping peak structure is so dense that many resonances occurring close together in frequency produce the appearance of a broad band.

In a recent comment, Birch and Yarwood {1} claim to have repeated some measurements by G. J. Evans {2-4} on liquid acetonitrile, but did not refer to the key paper by Coffey et al. {5}. Nor did they refer to the experimental paper of G. J. Evans {8} in which structure was clearly resolved in nematogenic liquid crystals, and the effect of

magnetic and electric fields on these nematogens carefully evaluated. The reproducibility of the data by G. J. Evans {8} was demonstrated by reference to a single crystal of anthracene {8}. The present paper is a reply to the comments made by Birch and Yarwood, comments which were not communicated to the present authors in preprint or reprint form. This lack of communication is surprising in view of the claim by Birch and Yarwood (p. 222 of ref. {1}) that their work was intended "as a check on earlier work" of G. J. Evans {2-4}.

1. REPLY TO EXPERIMENTAL COMMENTS.

The data on acetonitrile produced by Birch and Yarwood {1} have a quoted uncertainty of 10 to 20 wavenumbers. Presumably this means that the uncertainty in the measured power absorption coefficient was up to ± 20 neper cm^{-1} . It was claimed that the measured absorption spectrum was in good agreement with "the indirect measurements of the same study", presumably refractive indices {1}. It appears therefore that the uncertainty in the latter was equivalent. On the basis of these data it is asserted {1} that if discrete features were present in the far infra red spectrum of liquid acetonitrile "they must be less intense than the levels implied by the random uncertainties in the measurements". It is claimed, finally, that these random uncertainties were less than the levels in the earlier studies, presumably those of G. J. Evans {2-4}. Apparently, these comments are meant as scientific criticisms, although there has been no direct communication with the present authors. The latter reply as follows.

1) The structure obtained by G. J. Evans {2} in liquid acetonitrile was not random but reproducible and repeatable. The data in which peak structure was most prominent were not

obtained in acetonitrile, but in liquid crystals subjected to electric and magnetic fields { 8 }.

Birch and Yarwood {1} do not refer to this work.

2) The large uncertainty of up to ± 20 neper cm^{-1} in the data of ref. {1} means that no conclusion ~~can~~^{can} be drawn. The assertion that this uncertainty is less than that in the work of G. J. Evans {2-4} is unfounded and incorrect.

Referring to Fig. (2) of ref. {2} by G. J. Evans it is immediately obvious that the noise level is less than that published in Fig. (5.3.12) of ref. {1}. This makes nonsense of any claim to the contrary in ref. {1}. It is mentioned in ref. {2} that "Yarwood et al. do not appear to resolve the same detail, which could be the consequence of their averaging procedure in obtaining the spectrum, and any consequent data reduction." The key feature reported in ref. {2} is structure near 103 cm^{-1} , the presence of which is indicated by two independent measurements with a submillimetre laser, and by interferometric data {2}. The two laser points are at $270 \text{ neper cm}^{-1}$ (G. J. Evans) and $320 \text{ neper cm}^{-1}$ (Reid). These were obtained with independent apparatus and by different scientists, working independently. Both points are well below the level obtained by Ohba et al. {9}, and quoted in ref. {1}. The result of Ohba et al. {9}, however, was obtained at below 100 cm^{-1} , whereas those in Evans' paper {2} were at 103 cm^{-1} . These details are ignored by Yarwood and Birch {1}, who also fail to mention that the peak structure just described in pure acetonitrile disappears in solutions of thereof, as demonstrated by the very high quality of the data by G. J. Evans in his own paper {2}. As a "check" on ref {2}, ref. {1} is worthless, because the noise level in ref. {1} is higher than that in ref. {2}.

Furthermore, Yarwood and Birch {1} do not refer at all to the paper by G. J. Evans {8} in which peaks were observed unequivocally in nematogens. Yarwood and Birch are not

objective therefore in their scholarship, they do not take account of data which do not support their point of view. The latter appears to be based on a subjective assertion that no peaks can exist in the far infra red. In ref. {8}, G. J. Evans demonstrates reproducibility with reference to the far infra red power absorption of a single crystal of anthracene (his Figure 7). The paper demonstrates reproducible and repeatable peak structure in nematogens, structure induced by magnetic and electric fields and by dipolar solutes. These new modes are assigned unequivocally and distinguished from phonon modes. The peak detail is well resolved throughout the spectral range. The intensity and frequency of the new modes were controlled by magnetic and electric fields.

2. THEORETICAL REPLY.

Although available in the literature for four years prior to their publication, Yarwood and Birch {1} do not refer to the key paper by Coffey et al. {5} which shows analytically and numerically that peak structure in the far infra red emerges from the simple itinerant oscillator model {7}. For reference, the most important features of the theory are given in this reply. The original work also discussed conditions under which the peaks are expected: a) to be prominent; b) to be resolved; c) to be unresolved.

The peaks emerge from the double transcendental form of the orientational correlation function of the itinerant oscillator expressed in terms of Dirac delta functions premultiplied by modified Bessel functions, which determine their amplitudes. The delta functions represent frequencies in the far infra red spectrum of liquids around which resolved peaks may be observable under optimum conditions. In the simplest type of itinerant

oscillator, there is one such fundamental frequency and a theoretically infinite number of higher harmonics, of which a few are clearly resolved {5}. In terms of power absorption coefficient, the resolved fundamental and harmonics dominate the spectrum under the optimum physical conditions, and are clearly seen {5} even in terms of dielectric loss. (Usually, {7}, the far infra red region in terms of dielectric loss is observable as a small high frequency adjunct to the Debye type bell shaped curve at microwave and lower frequencies.)

In itinerant oscillator theory, therefore, far infra red peaks are **fundamental** to any appreciation of molecular dynamics, because they represent the librational motion of molecules in a cage of neighbours. Whether or not these peaks are resolved depends entirely on the physical conditions. In liquid crystals, it is likely that they are resolved, because the structure seen by G. J. Evans {2-4} is prominent in the far infra red.

DISCUSSION

The putative criticisms of Yarwood and Birch {1} appear to rely on spectra that are uncertain on the average by to up to about ± 20 neper cm in power absorption. These spectra are reported in their figure (5.3.12). However, the figure caption attributes this work to Ohba et al. {9}, apparently in error. It appears that the laser points are by Ohba et al. {9}, and the interferometric data by colleagues of Yarwood and Birch {1, 10}. The spectrum shown by Yarwood and Birch {1} is apparently one unaveraged run, but this is not clear. **It is, however, richly structured with peaks especially in the 120 to 150 cm^{-1} region, where they appear to be regularly spaced as in the theoretical spectra of Coffey et al {5}. The amplitude of some individual peaks, furthermore, is, on the average, much higher than the quoted uncertainty of 10 to 20 neper cm^{-1} .** The peak structure also appears in the refractive index

data {1} presented by Birch and Yarwood. This figure shows five points obtained by laser spectroscopy, with uncertainty bars. The uncertainty in the point at just ~~over~~^{under} 100 cm⁻¹ is about 100 neper cm⁻¹. The authors claim that their data, which qualitatively confirm the peak structure observed by G. J. Evans {2-4} must be random noise. There is no further discussion of why this conclusion should have been reached. The laser points are spaced apart by as much as 30 cm⁻¹, and clearly cannot be used either to confirm or disprove the existence of peaks.

Birch and Yarwood {1} claim that the data of Ohba et al. {9} amount to a "further independent confirmation of the absence of discrete features" in the far infra red spectrum of liquid acetonitrile. However, in the very next sentence {1} it is revealed that Ohba et al. {9} obtained **only six frequency points**. It is absurd to claim that these six points confirm the absence or presence of peak structure, because the resolution is far too low. The points by Ohba et al {9} are presented in Figure (5.3.12) as being in "excellent agreement" with those of Birch et al. {1,10}. The large uncertainties from both sets of measurements preclude the description "excellent agreement". A key laser point (near 100 cm⁻¹) obtained by Ohba et al. {9} has a published uncertainty of over 100 neper cm⁻¹. The mean uncertainty by Birch et al. {1,10} is published as about 10 to 20 neper cm⁻¹.

The well resolved peak structure given by Birch and Yarwood {1} in the 130 to 150 cm⁻¹ region of their Fig. (5.3.12) in liquid acetonitrile deserves some objective interpretation. There is no a priori evidence from this Figure that these regularly spaced peaks are random. There are ~~at~~^{at} least five regularly spaced peaks, separated by about 10 cm⁻¹. The sample thickness is not reported by the authors {1}, but for such a heavily absorbing sample it cannot be greater than about 0.1 mm. If these regularly spaced peaks were due to

interference patterns {11} set up by the windows of the cell, they would be spaced by about the inverse of the sample thickness, i.e. not less than 100 cm^{-1} . The peaks cannot therefore be attributed to this cause, and are evidently not random in nature. If they were random they would not be regularly spaced. Furthermore, the same type of regularity appears on this high frequency shoulder in the refractive index spectrum of Fig. (5.3.12). Finally, the theoretical {5} peak structure also appears on the high frequency side of the fundamental frequency, because the higher frequency peaks are higher harmonics. An objective analysis leads away from the assertion that the structure in the spectra obtained by Birch and Yarwood is random.

The theory of the itinerant oscillator allows peak structure, made up of a fundamental frequency and higher harmonics. When there is more than one fundamental frequency there is more than one set of higher harmonics, so that a realistic model of the liquid state would produce a large number of peaks, closely spaced in frequency. Insufficient instrumental resolution would not allow these to be resolved. In particular, it is absurd to claim that six laser points, spaced by as much as 30 cm^{-1} , allow a test of the reality of far infra red peaks. The data actually presented by Birch and Yarwood {1} confirm the presence of far infra red peaks, but these are asserted by the authors to be noise, presumably because they are not reproducible. From the single sample spectrum presented by Birch and Yarwood, it is not possible to see whether their spectra are or are not reproducible. The data presented by G. J. Evans {2-4} on the other hand, are reproducible and repeatable on the apparatus used by him. Theory {5} shows the presence of peaks {5}, and these are fundamental to the nature of the itinerant oscillator model of the liquid state.

In Fig (5.4.11) of the same article {1}, Birch and Yarwood present a smoothed far infra red spectrum of liquid acetonitrile, together with theoretical analysis taken from the

work of M. W. Evans et al. {11a, Fig. (6.3.2.14), 12}. The caption of this Figure, however, attributed the work to Yarwood {13}, and neither does this article^[13] nor the caption itself refer to the earlier work of M. W. Evans et al. {11a, Fig. (6.3.2.14), 12} from which the Figure was prepared. This smoothed, broad band, spectrum is typical of the way such data were presented before the work of G. J. Evans {2-4} concentrated attention on the underlying peak structure. The smooth appearance of such a spectrum is the result of a subjective curve drawing exercise. The actual data are discrete points, obtained from Fourier transform interferometry, by digital computation from an observed interferogram. The data presented by Birch and Yarwood {1}, and referenced to Yarwood {13}, originate in the work of M. W. Evans et al. {11a, Fig. (6.3.2.14), 12}. The theoretical curves in this Figure were computed originally by M. W. Evans and were published in refs. {11a} and {12}. It is surprising therefore that Birch and Yarwood {1} appear to be using data from the same laboratory (that of M. W. and G. J. Evans) as they are criticizing in another part of their article.

There are several other inaccuracies in the article by Birch and Yarwood {1} which in relation to the interpretation of the far infra red spectrum of acetonitrile. For example the three variables of Mori theory {11a} are referred to as "disposable parameters" whereas they are well defined in ref. {11a} in terms of molecular parameters such as mean square torque. The assertion (p. 260 of ref. {1}) that their physical meaning is "less than obvious" is not therefore correct. The models referred to by these authors are early analytical attempts at understanding the far infra red, which is now routinely modelled by computer simulation {14}. These misunderstandings underline a lack of comprehension which runs throughout the description of far infra red theory {11a} by these authors. There are basic inconsistencies, for example, on page 263, Fig. (5.4.13) is referred to {1} as describing a "number of solutions

of acetonitrile", but the Figure (on page 264) contains only two curves, described in the caption as "observed and fitted" far infra red absorptions of methyl iodide. The caption does not make clear which is the observed curve. If this is the solid curve, it is **richly structured with peaks**. According to standard theory {5} this is plausible.

Recently, Ohba and Ikawa {15} have published a far infra red spectrum of liquid acetonitrile based on a synchrotron radiation source. Fig. (1) of Ohba and Ikawa {15} shows a **regular peak structure** in the region from about 10 cm^{-1} to 200 cm^{-1} , but which does not extend throughout the spectrum to higher frequencies. Notably there are peaks at about 50 cm^{-1} , 80 cm^{-1} , 110 cm^{-1} , and about 140 cm^{-1} . The one at 110 cm^{-1} appears to coincide with that reported by G. J. Evans {2}. The regularity is reminiscent of the harmonic structure reported in ref {5} using the itinerant oscillator {5}. **The reported uncertainty {15} is far smaller than the peak amplitudes**. Unfortunately, these features are ascribed by Ohba and Ikawa {15} to interference within the 50 micron liquid layer. The basis for such a conclusion is not given, and it is not known whether or not these authors systematically attempted its removal by wedging the windows {15}, a standard far infra red technique reported in an early Thesis such as that of G. W. F. Pardoe {referred to in ref. (11) for example}. In Pardoe's Thesis, these interference peaks are separated by about the inverse of the path length. For 50 microns, this is about $2,000\text{ cm}^{-1}$! Any systematic interference pattern would also appear throughout the spectrum, but the peaks reported by Ohba and Ikawa {15} do not extend above 150 cm^{-1} . Ohba and Ikawa {15} assert that they are due to uniformity of angle of incidence, "having not been reported so far to our knowledge". Presumably, this means^{ns} that their origin is unknown. The analytical relation between this and the peak structure is not given. Significantly, these authors mention on page 991 {15} that the silicon discs used as

windows were slightly wedged. If this is the case, an analysis such as that of Pardoe {11} would show that any interference artifact would be removed. A good experimental example and thorough discussion of this artifact is given by Baise {16}.

The interpretation of the spectrum by Ohba and Ikawa {15} is based on a seven parameter fit of Mori type. There is, not surprisingly, a good agreement with data, but with seven parameters they could hardly fail. In an accompanying paper, Ohba et al. {17} report a computer simulation of liquid acetonitrile which is in good agreement with previous simulations, including one by M. W. Evans {18}, which was initially meant to check on the work of G. J. Evans {2}. It is significant that a series of recent computer simulations using the field applied molecular dynamics method {19} has revealed a richly structured spectrum of peaks in the far infra red region for molecular liquids subjected to torques, for example electric, magnetic and electromagnetic. This structure appears through rotational velocity autocorrelation functions in the picosecond time window.

Rodriguez and McHole {20} have recently obtained novel far infra red spectra of liquids in which the work of G. J. Evans {2} is referred to objectively. Polimeno and Freed {21} have referred objectively to the work of Coffey et al. {5} and have developed a multidimensional Fokker Planck Kramers theory for rotational relaxation of ^s small solutes in complex liquids in which the collective effects described by G. J. Evans {2-4,8} are explicitly represented by rotating torques and stochastic fields. The algorithm of Polimeno and Freed is probably capable of generating far ^{ra} infra red peaks in ^{re} the same way as that of Coffey et al. {5}, but this should be checked.

CONCLUSIONS

The work of Birch and Yarwood {1}, not communicated to the present authors, is worthless as a check on the work of G. J. Evans {2-4,8}. The most significant data of G. J. Evans {8} are not considered at all, and Birch and Yarwood also ignore the key theoretical work of Coffey et al. {5}, and of Polimeno and Freed {22}. The laser spectroscopic data reported in ref. {2} was compared {1} with the laser work of Ohba et al. {9}, but the most relevant laser point reported by these authors was uncertain to more than $100 \text{ neper cm}^{-1}$. The latest synchrotron data of Ohba et al. {17} show clearly the presence of far infrared peaks in pure liquid acetonitrile. The spectrum presented by Birch and Yarwood is also rich in peak structure {1}, but the latter is asserted by these authors to be noise. If the structure seen by Birch and Yarwood {1} is real, then the findings of G. J. Evans {2-4, 8} are confirmed qualitatively, if the structure is indeed noise, then the spectra obtained by Birch and Yarwood are more noisy by far than those obtained by G. J. Evans {2-4, 8}, and the "check" by Birch and Yarwood is worthless.

The theory of Coffey et al. {5}, which confirmed the plausibility of peak structure in the far infra red, was not referred to by Birch and Yarwood {1}, and neither was the theory of Polimeno and Freed {22}. Birch and Yarwood {1} have not to date proposed an alternative theory of their own, but rely on models (and diagrams) by other workers {1}. Finally, no attempt was made by Yarwood or Birch to communicate with the present authors during this "check", and the present authors were not aware that the "check" was taking place. The editors of ref. {1}, Steele and Yarwood, did not invite the present authors to reply to the comments made in ref. {1} by Birch and Yarwood, and no preprint of those comments was

forwarded to any of the present authors. The present article is a considered reply to the assertions of Birch and Yarwood {1}.

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