

INTERMOLECULAR DYNAMICS IN FLUIDS AND PLASTIC CRYSTALS

Submitted to the University of Wales in
candidature for the degree of Doctor in Scientia
by
Myron Wyn Evans, B.Sc., Ph.D.

Acknowledgements

I wish to thank the following for their aid over the last few years.

- (i) The staffs of the chemistry departments at Aberystwyth, Nice, Nancy, Oxford; N.P.L., and the Post Office.
- (ii) The computer staffs at Aberystwyth, Oxford, London and Manchester.
- (iii) Co-authors for their friendship and hard work.
- (iv) Fellow students in the class of 1971.
- (v) Editors, referees, publishers and printers.

STATEMENT

The articles numbered one to four below in the list of works have been submitted in candidature for the degree of Philosophiae Doctor. A chapter of this thesis has been used as the basis for the mathematical parts of articles nine, ten, and twelve. No part of the total work below is being submitted or has been submitted in candidature for any other degree except the above.

Signed... M. W. Evans

Date... 23rd. April, 1977

ABERYSTWYTH

SY23 1NE

(Telephone 0970 7645)

Edward Davies Chemical Laboratories

Professors: John M. Thomas
(Head of Department)
Mansel Davies



Adran Gemeg

Athrawon: John M. Thomas
(Pennaeth)
Mansel Davies

Declaration

To whom it may concern,

The articles listed below were prepared by me except for those numbered eleven, twelve, thirteen, eighteen, and forty-two. My roles in these latter are defined below and in the statements of the co-authors involved.

Article eleven

Here I was responsible mainly for the far infra-red data collection in the range above ten wavenumbers, and for the theoretical analysis thereof. Parts of this article were written by me, the major part of it by Dr. Jose Goulon.

Article Twelve

Dr. G.J. Davies was responsible for the data collection in the range below about ten wavenumbers. He wrote the section on model calculations and parts of the experimental section.

Article Thirteen

Here I was responsible for preparing the major part of the introduction and for all facets (theoretical and practical) of the far infra-red work.

Article Eighteen

In this review Prof. J. S. Rowlinson prepared sections one to four inclusive. The rest was prepared by me.

Article Forty-two

Here Dr. A.R. Davies was responsible for the mathematical generalisation of the Fokker/Planck equation, I was responsible for its application to molecular dynamics in the spectroscopic regime.

Signed... *M. W. Evans*

M.W. Evans, British Ramsay Fellow,

Date... *24th April, 1977*

Research 1971 - 1976

My original results and conclusions from the five past years can be listed as the separate items below. The state of knowledge beforehand is indicated briefly for each section.

(i) The use of Mori hydrodynamic and Kubo fluctuation-dissipation formation in interpreting absorptions in the far infra-red frequency region ($2 - 200 \text{ cm}^{-1}$; 60 GHz upwards) has proved revealing. It has been realised that this experimentally difficult spectroscopic region, opened up prior to 1971 by advances primarily in computer technology, represents only the short time part of one particular statistical property of a typical ensemble of molecules in the fluid condition. That property is the orientational correlation function $c(t)$. My work in this area has been to test various approximations to $c(t)$ using far infra-red data in combination with those at lower frequencies, namely the dielectric loss (ϵ'') and permittivity (ϵ'); together with some complementary Rayleigh scattering data. Two of the most important, coherent theories of condensed phase molecular dynamics and interactions to emerge in recent years have been those of Kubo and Mori, which predict a series of fundamental integro-differential equations linking $c(t)$ to memory functions $K_0(t), \dots, K_n(t)$. Knowledge of the initial decay of $K_n(t)$ with time t would be enough, theoretically to generate the whole time dependence of $c(t)$, and thus the far infra-red/lower frequency absorption and dispersion. Since short-term effects are associated via a Fourier transform with high frequency phenomena, the far infra-red is particularly well adapted as a probe into the rapidly decaying functions $K(t)$. It has the further advantage that the absorption coefficient observed, $\alpha(\omega)$ (neper cm^{-1}), is equivalent to (loss x frequency) and thus magnifies absorptions which

in loss representation would be faint high frequency shoulders. Further, $\alpha(\omega)$ is equivalent to Rayleigh depolarised scattered intensity multiplied by ω^2 , so that we have great advantages over this technique (currently much more popular) at high frequencies.

We have shown by propitious use of far infra-red data that an exponential $K_1(t)$, the basis of 'three variable' formalism, which emerged in the early 1970's, is successful only in very few, favourable cases, and generally it has been found that the far infra-red and microwave, used in combination, present a stern test of any theory which is apparently satisfactory in either frequency region alone, or when used to fit more insensitive effects such as the far wings of Rayleigh and Raman bands. This is because the microwave details the long time part of $c(t)$, and the far infra-red the short, so that in combination a fine composite picture of the orientational dynamics (or trochilics) is developed. This is apparent with the use of data at one temperature only; those at different number densities (N) and temperatures will be more penetrating. The simultaneous use of more than one experimental technique on one suitable fluid over a range of conditions will be more revealing still.

Recent computer experiments we carried out via the Aberystwyth to Manchester (U.M.R.C.C.) link have produced functions akin to $K_1(t)$ which are complicated and oscillatory in form and not remotely exponential, thus consolidating the indications obtained by the use of electromagnetic absorptions and dispersions as above. Future work will be concerned with trying to build up a sound theoretical framework upon which to base the interpretation of the vastly improved experimental data now being produced from a recently granted Mark III interferometer. We hope to use data over most of the 14 decades observable at Aberystwyth and also those from other techniques such as ^{13}C N.M.R. relaxation, and Raman/

Rayleigh scattering, which yield correlation functions similar and complementary to $C(t)$. It was to assist in this that we set up the programme of molecular dynamics computer runs where assemblies of simple potentials are studied with Newtonian laws of motion.

Mesophases of certain axially anisotropic molecules embody limiting features of trochilical motion as a result of this individual geometry. We were the first to exploit this using an interpretation of data in the far infra-red² in 1972, and recently we have seen in the nematogen 4-cyano-4 n-heptyl biphenyl (HCB) indications of a double loss phenomenon consisting of a Debye type curve at MHz frequencies linked analytically to a very sharp far infra-red band at about 140 cm^{-1} (THz frequencies) by a version of the Mori series. This is an extreme form of the same phenomenon clearly observable in the plastic crystalline phase of disk-like molecules such as trichlorotrimethylbenzene (TCTMB), but up to now it was not realised that these two experimental loss peaks are manifestations of the same overall time correlation function $C(t)$. The experimentally much better defined bands in TCTMB can be used as a very stringent test of any current theory of purely rotational Brownian motion, rotational coupling being restricted severely by virtue of the crystalline nature of the specimen. It is encouraging that even the approximate three-variable theory has proven sufficiently general to cover both extremes:

(a) the plastic crystal, with translation virtually absent on our time scale and rotational diffusion apparent; (b) the mesophase with rotational diffusion severely anisotropic and translational freedom retained. Both phases exhibit a long range ordering over and above that of the isotropic fluid - an ordering which has the effect of splitting the loss curve into two, one part synonymous with high frequency resonant torsional

oscillation in deep, steep intermolecular potential wells, the other being the blurred image of this motion (classical rotational diffusion against a continuum friction) as seen by the lower frequency dielectric probes.

In 1971 it was realised that the far infra-red was a high frequency adjoint to the classical microwave Debye absorption/dispersion, but little effort had been made to use the available data as a test for generalized theories of Brownian motion, and further to interlink these results with those of other relaxation experiments. The data themselves were often uncertain to the extent of \pm (10-15)% of $\alpha(\omega)$, and subtleties such as solvent effects (cross-correlations) were practically impossible to discern. With our new Mark III instrument we are discovering these small changes observable in the microwave, and thus by the nature of $c(t)$ ought to be there in the far infra-red. We are now ready to evaluate orientational cross-correlation functions.

(ii) I feel that my most satisfactory contribution has been in the interpretation of the interaction induced far infra-red absorptions of non-dipolar liquids (and to a lesser degree, Rayleigh depolarised scattering in molecules or atoms with scalar polarisabilities). It proved useful to express these bands as a sum of auto and cross-correlations of these dipoles (or induced polarisabilities) which for each individual molecule (or atom) vary in both magnitude and direction with time. This sum may then be expanded in a series of memory functions as for permanent dipolar absorption and the result Fourier transformed back to the frequency domain. The end product is a very fine fit to the available data over a range of temperatures, molecular number densities, and molecular geometries. The fitting procedure yields an experimental mean square torque factor ($K_i(o)$), the variation of which under the experimental

conditions above may be simulated again with suitable computer ensembles (about 10^2 molecules) of spherical or dumbbell potentials. The factors $K_1(o)$ gleaned from both techniques vary in much the same fashion with T or N, so that the looked-for coherence is beginning to appear. Prior to 1971 the attempts at the interpretation of such absorptions in liquids were based on the point-multipole field expansion used in a quantum theory of bimolecular, collision-induced dipole absorption in gases.

iii) These attempts were unsuccessful in liquids because of the multi-molecular nature of the interactions therein, but in moderately compressed gases of simple dipolar and non-dipolar molecules the far infra-red collision induced band is virtually bimolecular in origin and contains valuable information on the attractive (electrostatic) as well as the repulsive (overlap) part of the intermolecular potential. We exploited this by using a very highly quadrupolar molecule, cyanogen, and found that quadrupole-quadrupole interaction, neglected in the available quantum theory, is responsible for an anomalously high value of the quadrupole moment needed to match the experimental integrated absorption intensity.

The available theory was extended in conjunction with the theoretical physicist Frost to include general multipole induced dipole absorption in both linear and symmetric top molecules. The first successful use of the new theory was in interpreting the far infra-red induced band of oxygen with a combination of quadrupole and hexadecapole terms - an interpretation very recently (1976) endorsed by Birnbaum et.al. Our new theoretical capability has enabled us to interpret our results for the symmetric tops CCF_3 , CB_rF_3 and C_2F_6 at gaseous number densities commensurate with those of the liquids in some cases. It was concluded that in the first two, octopole induced absorption is important, and in the latter we have observed a high frequency wing where the hexadecapole absorption

is expected to appear. Before the contribution of Frost and ourselves in around 1972 there existed no theory for collision induced absorption except for linear and spherical top molecules. Future work will be concerned with an intercomparison of the classical Mori and quantum Frost formalisms.

List of Works Submitted

1. A far infrared study of propyne in the compressed gaseous, liquid and solution states*
Spectrochimica Acta, 1974, 30, 79 - 90.
2. Collision induced absorption in compressed gaseous cyanogen and comparison with the liquid phase absorption in the region 20 - 120 cm^{-1} .*
J. C. S. Faraday II, 1973, 69, 763 - 770.
3. Molecular motion and molecular interaction in the nematic and isotropic phases of a liquid crystal compound* (with M. Davies and I. Larkin).
J.C.S. Faraday II, 1973, 69, 1011 - 1022.
4. Interpretation of the microwave and far infra-red absorption of some dipolar liquids in terms of librational and relaxational motion.* (with I. Larkin)
J.C.S. Faraday II, 1974, 70, 477 - 482.
5. Rotational velocity correlation function for assessing molecular models for gas and liquid phase studies.
J.C.S. Faraday II, 1974, 70, 1620 - 1627.
6. Investigation of the Inter-molecular dynamics of non-dipolar molecules using the rotational velocity correlation function.
J.C.S. Faraday II, 1975, 71, 71 - 80.
7. Molecular dipole moments in the liquid phase: an assessment introducing the far infra-red dispersion.
Spectrochimica Acta, 1975, 31, 609 - 616.
8. M, J diffusion and torsional oscillation in CHF_3 and N_2O .
J.C.S. Faraday II, 1975, 71, 843 - 851.
9. Effect of $\Delta J = 4$ transition on the far infra-red normalised lineshapes of O_2 , CO_2 and $(\text{CN})_2$ gases.
J.C.S. Faraday II, 1975, 71, 1255 - 1261.

* Submitted in candidature for the degree of Philosophiae Doctor awarded in Dec. 1974. See this thesis for declaration of roles played by co-authors in refs 1. - 4. above.

10. Some equations for multipole-induced dipole absorption in linear molecules.
Molecular Physics, 1975, 29, 1345 - 1351.
11. Re-investigation of the methyl and methoxy group hindered rotations in p-dimethoxy benzene by comparison of dielectric and far infra-red spectra with ^{13}C N.M.R. relaxation data. (With J. Goulon, D. Canet and G. J. Davies).
Molecular Physics, 1975, 30, 973 - 995.
12. Far infra-red Manifestations of the intermolecular dynamics in compressed gaseous and liquid CClF_3 . (with G. J. Davies).
J.C.S. Faraday II, 1975, 71, 1275 - 1292.
13. Dielectric properties, refractive index and far infra-red spectrum of cholesteryl oleyl carbonate. (with R. Moutran and A. H. Price).
J.C.S. Faraday II, 1975, 71, 1854 - 1862.
14. Comparison in the time region 0 - 1.2 ps of model and experimental absorptions of liquid and rotator phases in the far infra-red.
J.C.S. Faraday II, 1975, 71, 2051 - 2064.
15. Model interpretations of the far infra-red absorptions in compressed gaseous and liquid bromotrifluoro methane, CBrF_3 . (with G. J. Davies)
J.C.S. Faraday II, 1976, 72, 40 - 53.
16. Models of the orientational autocorrelation function from far infrared absorption in liquid and rotator phases.
J.C.S. Faraday II, 1976, 72, 727 - 730.
17. A generalised friction model for the evaluation of angular momentum autocorrelation functions.
Chemical Physics Letters, 1976, 39, 601 - 605.
18. The Motion of simple molecule in liquids. (with J. S. Rowlinson)
Chemical Society Annual Reports A, 1975, 5 - 30.
19. Use of the memory function to simulate the Debye and Poley absorptions in liquids. (with G. J. Evans)
J.C.S. Faraday II, 1976, 72, 1169 - 1184.
20. Use of generalised Langevin theory to describe infrared absorptions in non-dipolar liquids. (with G. J. Davies)
J.C.S. Faraday II, 1976, 72, 1194 - 1205.

21. Effect of pressure and temperature on the intermolecular mean square torque in liquid CS_2 and CCl_4
(with G. J. Davies)
J.C.S. Faraday II, 1976, 72, 1206 - 1213.
22. An experimental study and classical treatment of the far infra-red induced dipolar absorption in gaseous ethylene
(with G. J. Evans)
Advances in Molecular Relaxation Processes, 1976, 9, 87 - 103
23. A simple model for the orientational correlation functions of dipolar and induced-dipolar absorptions in liquids
(with G. J. Davies)
Advances in Molecular Relaxational Processes 1976, 9, 129 - 152.
24. Rotational dynamics of CH_3Cl and CH_2CF_2 in the fluid state
(with G. J. Davies and G. J. Evans)
J.C.S. Faraday II, 1976, 72, 1901 - 1910.
25. Collisional line-broadening in far infrared induced dipolar absorption.
Spectrochimica Acta, 1976, 32, 1253 - 1258.
26. Use of the memory function to predict microwave/far i.r. rotational band shapes.
Spectrochimica Acta, 1976, 32, 1259 - 1263.
27. An extended fraction representation of the correlation function of induced absorption in liquid mixtures
(with G. J. Davies)
Chemical Physics Letters, 1976, 41, 521 - 524.
28. Quantised Rotation of HBr in liquid SF_6
(with G. Wegdam and G. J. Evans)
Chemical Physics Letters, 1976, 42, 331 - 334.
29. Reorientation of Water molecules free from hydrogen bonding.
J.C.S. Faraday II, 1976, 72, 2138 - 2146.
30. Rotational Brownian motion in liquid and plastic crystalline CBr_4 from far infrared induced absorption
(with G. J. Davies and G. J. Evans)
J.C.S. Faraday II, 1976, 72, 2147 - 2154.
31. The Mori formalism, a critical discussion of its use in representing far infrared and microwave absorptions
(with G. J. Evans)
Chemical Physics Letters, 1977, 45, 454 - 459.
32. High and low frequency torsional absorptions in nematics K21
(with G. J. Evans)
J.C.S. Faraday II, 1977, 73, 285 - 292.
33. Truncated series expansion for the correlation function of permanent and induced depolarised Rayleigh bands.
J.C.S. Faraday II, 1977, 73, 485 - 492.

34. The absorptions of dipolar liquids in the far infrared: a sensitive measure of the Mori continued fraction.
(with G. J. Davies and G. J. Evans)
J. C. S. Faraday II, 1977, in press.
35. The properties of some derivative a.c.f.'s computed with the atom-atom potential.
(with G. H. Wegdam and G. J. Evans)
Molecular Physics, 1977, in press.
36. A computer simulation of the dynamical properties of diatomic fluids.
(with G. H. Wegdam and G. J. Evans)
Advances in Molecular Relaxation and Resonance Processes, 1977, in press.
37. The itinerant oscillator treated and extended in terms of the Mori continued fraction.
Chemical Physics Letters, 1977, in press.
38. The Calculation of the orientational ~~form~~ ^{function} on oscillatory angular velocity a.c.f.
Molecular Physics, 1977 (being refereed).
39. Correlation and Memory Function Analyses of Molecular Motion in Fluids.
A chapter for 'Dielectric and Related Molecular Processes' Vol. 3, 1977 - a Chemical Society Specialist periodical report; in press.
40. Recent Developments in the Statistical Treatment of Molecular Relaxation in the Condensed Phase.
A review to be published in March 1977 in Advances in Molecular Relaxation and Resonance Processes, Vol. 10.
41. Hexadecapolar absorption in compressed C_2F_6 .
(with G. J. Davies)
J.C.S. Faraday II, (being refereed).
42. A generalised Fokker/Planck equation for Brownian motion of the general dynamics variable
(with A. R. Davies)
Molecular Physics (being refereed).

Curriculum Vitae

1. Pontardawe G. S. (now Cwmtawe Comp.).
2. 1968 - 1971, U.C.W. Aberystwyth
1969 Matthews Prize.
1971 B.Sc. (Class 1).
3. 1971 - 1974, U.C.W. Aberystwyth
Funded as top first by a Dr. Samuel Williams studentship.
April - Aug. 1973, three months with Prof. C. Brot at the
Univ. of Nice, and Prof. J.-L. Rivail at the Univ. of Nancy.
During this period a frequent guest worker at the N.P.L.,
and the P.O. Telecommunication H.Q., researching with
Dr. G. J. Davies.
1974 - Ph.D., under Prof. M. Davies.
4. 1974 - 1976, S.R.C. post doctoral fellow with
Prof. J. S. Rowlinson at the Univ. of Oxford Physical
Chemistry Laboratory. Offered an I.C.I. European
fellowship and a N.R.C.C. fellowship.
5. Elected Junior Research Fellow of Wolfson College in 1975.
Awarded S.R.C. apparatus grant No. B/RG/83985 (£10,000).
6. 1976 - Awarded the Ramsay Memorial (British) Fellowship
for 1976 - 1978; together with travel grant No. GR/A/06570
(attached), jointly with Prof. M. Davies. Invited
speaker to a Gordon Research Conference.
7. 1977 - Awarded S.R.C. grant for a post-doctoral worker,
jointly with Prof. M. Davies. Invited speaker to the
European Spectroscopy Union Conference at Wrocław, Poland.
Apparently reached standard necessary for the Marlow
medal of the Chemical Society (see ref. attached).



GORDON RESEARCH CONFERENCES

PASTORE CHEMICAL LABORATORY
UNIVERSITY OF RHODE ISLAND
KINGSTON, RHODE ISLAND 02881
November 14, 1975

ADDRESS REPLY TO:

Dr. Myron Evans
c/o Prof. J. S. Rowlinson
Physical Chemistry Department
Oxford University
Oxford, GREAT BRITAIN

Prof. Worth E. Vaughan
Department of Chemistry
University of Wisconsin-Madison
Madison, Wisconsin 53706

Dear Dr. Evans:

I am in the process of constructing the program for the 1976 Gordon Conference on Dielectric Phenomena which will be held July 26-30, 1976 at Proctor Academy, Andover, New Hampshire, USA. Part of the Conference will be devoted to sessions tentatively called "Dielectric processes and intermolecular forces in fluids". The emphasis will be on analysis of experimental data via correlation function methods and interpretation of alternative models of the molecular motion. Your recent research seems most relevant to this topic.

I would like to invite you to speak at the Conference. Please let me know if you are able to accept.

Regarding financial support, the Conference has a fund which is used to provide assistance to attendees. Pressure on this fund is large. However, I am able to pay the fixed fee for the conference (\$160 covering registration, meals, room) and to contribute to travel expense (\$340 additional say) for a total subsidy of \$500. I hope this will be sufficient to allow you to attend the Conference.

Although the whole program is not yet firm, topics likely to be included are theory of dielectric relaxation in polar media, thermally stimulated depolarization, instrumentation and measurement, conducting dielectrics, effects of high fields on dielectric processes, dielectric processes and intermolecular forces in fluids, Monte Carlo studies of dielectric behavior, and new horizons in dielectric research. I believe much of this will interest you.

I hope you will be able to contribute to the Conference program.

Sincerely,

Worth E. Vaughan
Chairman, 1976 Gordon Conference
Dielectric Phenomena

XIIIth EUROPEAN CONGRESS ON MOLECULAR SPECTROSCOPY
WROCLAW, 12 - 16 SEPTEMBER, 1977

Chairman:
Professor B. Jeżowska-Trzebiatowska
Vice-Chairman:
Professor H. Ratajczak
Scientific Secretariate:
Dr. J. Drożdżyński
Dr. J. Legendziewicz
Dr. Z. Mielke

Address replies to:
Organizing Committee
of the XIIIth E.C.M.S.
Institute of Chemistry
University of Wrocław
14 Joliot-Curie Street
50-383 Wrocław, Poland
Telephone 229281
Telex 402-303 (University, Wrocław)

Dr. Myron Evans
Edward Davies Chemical Laboratories
Aberystwyth, SY23 1NE
U.K.

17th February, 1977

Dear Dr. Evans,

The Spectroscopy Committee of the Polish Academy of Sciences is organizing the XIIIth Congress on Molecular Spectroscopy in Wrocław, 12-16 September, 1977.

The purpose of the Congress is to discuss the progress in the theoretical and experimental spectroscopic investigations of molecular systems, in particular, in the following areas:

1. Molecular dynamics and interactions in liquid, molecular crystals, liquid crystals and molecular complexes.
2. Spectroscopy of metal ions in complexes and biological systems.
3. Spectroscopy excited electronic states in molecular and ionic systems.
4. Spectroscopy of simple molecules /high resolution spectroscopy/.
5. Methodological and instrumental innovations.

However by the invited lectures we should like to cover also other fields or molecular spectroscopy.

On behalf of the Organizing Committee we have the honour to ask you, as an established scientist, to present an invited lecture /30 min/ in the field of molecular dynamics in liquid.

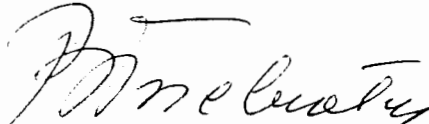
We would highly appreciate if you would kindly accept this invitation and inform us on the preliminary title of your lecture as soon as possible.

Unfortunately, so far our budget has been unstable so at present we can not offer you any financial support. However we will do our best so that your expenses in Wrocław could be covered by the Organizing Committee.

With very best regards,

Yours sincerely


Henryk Ratajczak


B. Jeżowska-Trzebiatowska



Science Research Council
State House High Holborn London WC1R 4TA

Telex 25962

Telephone 01-242 1262 ext 120

Professor Mansel Davies
Edward Davies Chemical Laboratories
University College of Wales
Aberystwyth
SY23 1NE

Your reference

In reply please quote
GR/A/06570

Date
26 MAR 1976

Dear Professor Mansel Davies

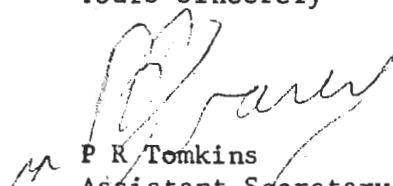
RESEARCH GRANT: MOLECULAR MOTION IN LIQUIDS

The Council has now been able to consult its Committees on the above application, and I am pleased to tell you that an award of £550 was recommended.

The Chemistry Committee in considering your application, involving support for Dr Myron Evans, recognised that he is an outstanding young chemist and was impressed by the programme of work proposed. It noted however that he will be supported for the next two years on a Ramsey Memorial Fellowship, and therefore the Committee recommended travel support only for that period. If Dr Evans has not obtained a permanent position by the end of his Ramsey Fellowship, the Committee would be prepared to give sympathetic consideration to an application for his support at that time.

I trust that this award is acceptable to you, and on this assumption I enclose a copy of the Council's official letter to the Registrar announcing the award.

Yours sincerely


P R Tomkins
Assistant Secretary
Chemistry Committee



The Chemical Society

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memberships of
The Chemical Society,
The Royal Institute
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The Faraday Society
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Faraday Division
Professor F C Tompkins
DSc, CChem, FRIC, FRS

Burlington House
London W1V 0BN
Telephone 01-734 9971
Telex 268001

Dr. M. W. Evans
Edward Davies Chemical Laboratories
Aberystwyth SY23 1NE

10 March 1977

Dear Dr. Evans,

1977 Marlow Award

I am writing to inform you that the Awards Committee of Faraday Council have decided to award the Marlow Medal for 1977 to Dr. J. N. L. Connor of Manchester University. I have been asked to thank you for making an application and to tell you that the candidates were of extremely high quality this year and the Committee had great difficulty in choosing between them.

Since you will still be eligible for the award in 1978, the Council hope that you will permit your application to go forward for consideration again next year. In this case, perhaps you would like me to keep your reprints for the time being. You will, of course, be invited to add any more recent publications to the list at the appropriate time.

Yours sincerely,

F. C. Tompkins
Honorary Secretary

LAWRENCE BERKELEY LABORATORY

UNIVERSITY OF CALIFORNIA

BERKELEY, CALIFORNIA 94720 □ TEL. (415) 843-2740

February 3, 1976

Dear Sir,

I understand that Dr. Myron EVANS is being considered for the degree of "Doctor in Scientia" and I am very pleased to state his valuable contribution to our joint paper entitled :

" Reinvestigation of methyl and methoxy group hindered rotations in p.-dimethoxybenzene, by comparison of dielectric and far infrared spectra with ^{13}C N.M.R. relaxation data " - Molecular Physics (1975) 30 (4) 973-995 .

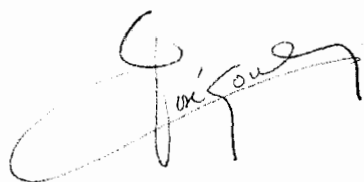
Dr. EVANS first came to the "Laboratoire de Chimie Theorique" (Universite de Nancy I - FRANCE) as a guest worker for six weeks in May 1973 and he was very quick to use the rather sophisticated interferometric techniques developed in this laboratory for dielectric relaxation studies at very high frequencies (8-120 GHz) in liquid phase. At that time, I was actively engaged in a program of experiments, the main goal of which was a better description of the dynamics of internal rotations in various non rigid molecules (e.g. diacetyl, methylal ...etc..) and I suggested to Dr. EVANS to reinvestigate the dielectric relaxation of paradimethoxybenzene, the non rigidity of which was not yet clearly defined. Due to the wholehearted dedication of Dr. EVANS to his work, we were able to obtain before he left Nancy, all the dielectric data quoted in the aforementioned paper, and also some yet unpublished data concerning pure dimethylcarbonate. Dr. EVANS also proposed to complete his experimental work in the microwave region by complementary far infrared measurements to be made in Aberystwyth (Wales - U.K.) or at the "Post Office Research Center" (Dollis Hill - London U.K.) in collaboration with Dr. Graham DAVIES.

Some months later, my colleague Dr. Daniel CANET and me working together obtained the set of ^{13}C N.M.R. relaxation data reported in the same paper. These allowed us to achieve an experimental definitive proof of the contribution of the methoxy group internal rotations to the observed dielectric relaxation process. They also allowed a quantitative analysis (tentative indeed!) of the dielectric relaxation phenomena in terms of a competition between a diffusional reorientation of the whole molecule and chemical relaxation processes corresponding to the rotational isomerisms.

I met again Dr. EVANS in Aberystwyth in February 1974 for a general discussion of our results. He made a number of most valuable suggestions concerning the interpretation of the far I.R. data and computed the so-called "pseudo" velocity correlation function. I also much appreciated his kind assistance in writing a first draft of the paper. Finally, further comments from Dr. Georges ROUSSY (Universite de Nancy I) concerning our analysis of the far I.R. data led me to extend the QUADE et al. formalism and to modify our discussion of the far I.R. data in order to include already in this paper some partial results of this still unpublished work (see reference 60).

In summary, there is no doubt for me that Dr. EVANS is a most able scientist with whom I greatly appreciated to work and I look forward to any further development of our friendly collaboration.

Your faithfully,

A handwritten signature in black ink, appearing to read 'Jose Goulon', written in a cursive style with a large initial 'G'.

Dr. Jose GOULON

THE UNIVERSITY COLLEGE OF WALES

COLEG PRIFYSGOL CYMRU

ABERYSTWYTH
SY23 1NE

(Telephone 0970 7645)

Edward Davies Chemical Laboratories

Adran Gemeg

Professors: John M. Thomas
(Head of Department)
Mansel Davies

Athrawon: John M. Thomas
(Pennaeth)
Mansel Davies



9th July, 1976.

Declaration

I declare that I carried out the refractive index, dipole moment, and dielectric relaxation measurements in the publication:

"Dielectric Properties, Refractive Index and Far Infrared Spectrum of Cholesteryl Oleyl Carbonate",
which appeared in the Journal of the Chemical Society, Faraday Transactions 2,
1975, 71, 1854.

The far infra-red spectra were taken and interpreted by Dr. M W Evans, who wrote the introduction, part of the experimental section, and pp. 1858 onwards from the heading, "Far Infra-red Measurements".

Signed,

Dr. R F S Moutran,
Research Fellow.

THE UNIVERSITY COLLEGE OF WALES

COLEG PRIFYSGOL CYMRU

ABERYSTWYTH
SY23 1NE
(Telephone 0970 7645)

Edward Davies Chemical Laboratories

Professors: John M. Thomas
(Head of Department)
Mansel Davies



Adran Gemeg

Athrawon: John M. Thomas
(Pennaeth)
Mansel Davies

24th April 1977

DECLARATION

To whom it may concern,

I declare that I was responsible for the dielectric and refractive index work in article thirteen. Dr. Evans undertook the collection and analysis of data in the far infra red.

Signed.....*A. H. Price*.....

A.H.Price, Senior Lecturer.

POST OFFICE RESEARCH CENTRE



MARTLESHAM HEATH
IPSWICH
IP5 7RE

Telephone: Ipswich 64 3477
STD Code: 0473
(Enquiries: Ipswich 643210)
Telex:
98376 (PO RESEARCH WBGE)
Giro a/c: 509 6715

In any reply please quote:

Your reference:

R3.1.1

I declare that in the following papers, the share of the work attributable to Dr M Evans is as indicated.

- 1 J C S FARADAY II, 1975, 71, 1275-1292

This paper was written in most part by Dr Evans, except for the section "Model Calculations". All the data recorded below 30 cm⁻¹ was my work.

- 2 MOL. PHYS, 1975, 30(4), 973-995

I endorse the statement drawn up by Dr Goulon.

- 3 J C S FARADAY II, 1976, 72, 40-53

This paper was written by Dr Evans. The original experimental data were obtained jointly, although the data recorded below 30 cm⁻¹ was my work.

- 4 J C S FARADAY II, 1976, 72, 1194-1205 and 1206-1212

These papers were written up by Dr Evans who was also responsible for some of the theoretical work involved. I was responsible for instigating the work and for all the experimental data used in the articles. The computation of certain correlation functions was also my work.

- 5 J C S FARADAY II, 1976, 72, 1901-1910

This article was written by Dr Evans, using original experimental data which, in the region below 30 cm⁻¹ were recorded by myself.

- 6 CHEM. PHYS. LETTERS, 1976, 41(3), 521-524

The idea for this article was mine as were some of the data used. The theoretical work is Dr Evan's.

- 7 J C S FARADAY II, 1976, 72, 2147-2154

The idea for this article was mine but was written by Dr Evans with my experimental collaboration and interpretive suggestions.

- 8 ADV. MOL. REL. PROC. 1976, 9, 129-152

This is a theoretical article written by Dr Evans using my original experimental data.

Dr G. Davies
22/4/77.

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Athrawon: John M. Thomas
(Pennaeth)
Mansel Davies

Statement

To whom it may concern,

In article 34 I was responsible for obtaining the experimental data below \approx 30 wavenumbers and for writing the experimental section on the original development of the polarising interferometer. In article 41 I was responsible for the experimental work in toto, Dr. Evans for the theory, introduction, and discussion.

Signed... *G. J. Davies*

Date... *31/5/77*

Dr. G J Davies

THE UNIVERSITY COLLEGE OF WALES

ABERYSTWYTH

SY23 1NE

(Telephone 0970 7645)

COLEG PRIFYSGOL CYMRU

Edward Davies Chemical Laboratories

Professors: John M. Thomas
(Head of Department)
Mansel Davies



Adran Gemeg

Athrawon: John M. Thomas
(Pennaeth)
Mansel Davies

19-9-1976

Declaration

In the following papers, the parts played by Dr. M W Evans were as indicated.

(1) J.C.S. Faraday 2, 1976, 72, 1169.

This paper was written by M W Evans, who developed the theory. I was responsible for the computation and curve fitting.

(2) J.C.S. Faraday 2, 1976, 72, 1901.

I endorse the statement made by Dr. G.J. Davies. In this article I was responsible for collecting the experimental data above 20 cm^{-1} , using some techniques developed jointly with M W Evans.

(3) J.C.S. Faraday 2, 1976, 72, _____.

This paper on CBr_4 was written by M W Evans, who developed the theory therein. I was responsible for the experimental side.

(4) Chem. Phys. Letters, 1976, 42(2), 331.

This was written jointly by G H Wegdam and M W Evans, who developed some of the theory presented. I collected the experimental data using a cell designed jointly with M W Evans.

(5) Adv. Mol. Rel. Proc., 1976, _____.

This paper was written by M W Evans, who developed the theory. I was responsible for the original experimental data.

Gareth J. Evans, B.Sc.

G. J. Evans

THE UNIVERSITY COLLEGE OF WALES

COLEG PRIFYSGOL CYMRU

ABERYSTWYTH
SY23 1NE
(Telephone 0970 7645)

Edward Davies Chemical Laboratories

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(Head of Department)
Mansel Davies



Adran Gerneg

Athrawon: John M. Thomas
(Pennaeth)
Mansel Davies

I declare that I was a junior author in papers 31, 32, 34, 35, and 36. I endorse the statement made by Dr. Wegdam.

G. J. Evans, B.Sc.

G. J. Evans

PHYSICAL CHEMISTRY LABORATORY
OXFORD UNIVERSITY

J. S. Rowlinson
Dr. Lee's Professor of Chemistry



SOUTH PARKS ROAD
OXFORD
OX1 3QZ
Oxford (0865) 53324

28th February 1977.

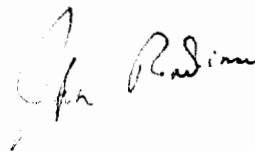
Dr. M.W. Evans,
Edward Davies Chemical Laboratories,
University College of Wales,
Aberystwyth, SY23 1NE.
Wales.

Dear Myron,

Thanks for your letter and for the three additional copies of our review. I have pleasure in confirming that you were indeed a joint author of "The Motion of Simple Molecules in Liquids" published in the Annual Reports of the Chemical Society for 1975, vol. 72A, page 5.

With best wishes.

Yours sincerely,



Dr. G.H. Wegdam

Dr. M. Evans
Edward Davies
Chemical Laboratories
Aberystwyth
Dyfed
U.K.

Nieuwe Prinsengracht 126
Amsterdam-C.

Telefoon 020 | 522.9111
.2327

Amsterdam, March 4th, 1977.

Dear Myron,

In your last letter you asked me to define my role in our joint project on molecular dynamics and in the work on HBr in SF₆.

In the molecular dynamics project I developed the programmes and did part of the "experimental" work, while you wrote the papers. In the HBr papers the roles were more or less reversed, you did the experimental work and I provided the theory for our joint paper.

If you have any comment on the content or phrasing of this definition, please let me know. Next week I will phone you to hear your remarks, if any.

Yours sincerely,

Gerard



Dept. of Applied Mathematics,

University College of Wales,

Aberystwyth,

DECLARATION

To whom it may concern,

I declare that in article 42 I was responsible for the mathematical physics and Dr. Evans for its application to chemical physics.

Signed... *A.R. Davies*

A.R. Davies, Lecturer in applied mathematics

Date... *29 April 1977*