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In Honour of Professor Dušan Hadži's 60th Birthday

FOREWORD

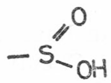
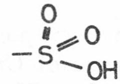
I am very pleased to have been asked to provide an introduction to this special issue of *Croatica Chemica Acta* in honour of professor Dušan Hadži's 60th birthday. We have been good friends since he spent a year in Cambridge in 1950—51, which was the year that I was first in charge of a research group of my own. During his subsequent career, among many other scientific activities, he has made an extremely important contribution to the understanding of the fundamental chemical problem of hydrogen bonding, a subject in which we jointly developed a spectroscopic interest some 30 years ago.

It can be said that scientific research is in Professor Hadži's blood, for his father Jovan Hadži was a distinguished Yugoslavian biologist. Dušan's Ph. D. work at the University of Ljubljana was concerned with the structure and properties of coal, particularly a sulphur-rich coal of economic importance to Slovenia. At that time infrared spectroscopy was in the process of developing into a wide-ranging technique for investigating molecular structure and had been applied by Sutherland and Cannon at Cambridge to the study of coal. When, with the encouragement of Professor Samec, the head of the Kemijski Inštitut Boris Kidrič, Hadži applied to join the Cambridge group for part of his Ph. D. work, he learnt that Sutherland was about to leave for the USA. However he was welcomed to join the research group, by then under my care, that was using the infrared equipment that Sutherland had left behind at Cambridge.

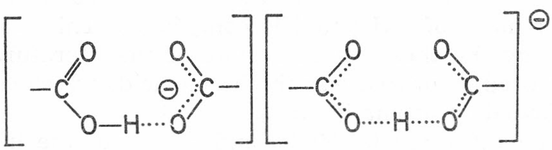
Hadži quickly mastered the, at that time still tricky, infrared spectroscopic techniques and he investigated the aromatic and oxygen-containing functional groups of coal. I had previously acquired some expertise in interpreting the infrared spectra of CH deformation modes of hydrocarbons and was interested to make similar studies of OH and NH compounds. This was a tougher proposition to judge by the then confused state of the literature. One important type of oxidation product of coal was the humic acids which contained multiple COOH groups bonded to aromatic rings.

This led to a joint study by Hadži and myself of the infrared spectra of COOH and COOD group (and later of chelated hydroxyquinones) in the OH/OD bond-stretching and angle-bending vibrational regions. This study was successful in explaining spectral complexities due to coupling of OH deformation and C—O bond-stretching modes. We also proposed an interpretation for sub-bands in the OH bond-stretching region of the infrared spectra of the COOH groups in terms of Fermi resonance with overtones and combinations of the coupled OH deformation and C—O stretching modes. With the ability, drive and enthusiasm of Dušan Hadži these objectives were successfully achieved and they have stood the test of time.

Hadži returned to Ljubljana to continue work for his doctorate. In the following period he published many more papers in coal research and built up his own research group. In due course he took delivery of the then new and very efficient Perkin-Elmer Model 21 double-beam infrared spectrometer. This was the first infrared spectrometer in Yugoslavia. He became increasingly interested in the infrared spectroscopic phenomena associated with hydrogen bonding. These fundamental researches, carried out over two and a half decades, led to a very high international reputation for his research school in Ljubljana.

One of the first structural problems that Hadži investigated, with Detoni, was concerned with the tautomeric structures of the sulphinic acids. At that time the alternative structural possibilities of  and  had not been resolved. The infrared spectra showed convincingly that the first structure is correct and that the OH hydrogen bonding is very strong. This and related work led to a general realisation that strong hydrogen bonding gives rise to very broad νOH bands, often with several maxima. These fall in wavenumber regions which are well below the 3300 to 2700 cm^{-1} range which at that time was normally assigned to hydrogen-bonded OH's.

Three broad bands were often found near 2700, 2300 and 1800 cm^{-1} (later designated by Hadži as A, B, C bands). In some extreme cases no bands attributable to OH bond-stretching vibrations could be found above 1600 cm^{-1}. In the latter cases a very broad continuum — often up to 1000 cm^{-1} broad — was observed below this wavenumber limit, sometimes with sharp superimposed minima. Albert and Badger at about the same time observed an example of this broad low-frequency continuum. These were some of the most unexpected and remarkable phenomena ever observed in infrared spectroscopy. With Novak, Professor Hadži showed that the spectra of acid salts of carboxylic acids e. g. CH_3COOH, $CH_3COO^-Na^+$, were particularly prone to give spectra of these extreme types, and that under these circumstances it was difficult to observe different C=O bond stretching frequencies related to separate —COOH and —COO^- groups. This suggested the presence of a symmetrical or near-symmetrical hydrogen-bonded system that could be approximately formulated as II rather than I below



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If not strictly symmetrical, the strong hydrogen bond could lead to rapid proton transfer between equivalent minima close to one —CO_2 group or the other. It was in fact suggested by Hadži and Blinc, in the context of studies of ferroelectric solid materials such as KH_2PO_4, that the several A, B, C maxima might arise from transitions between the multiple energy levels associated with tunnelling of the proton within a double-minimum potential energy function.

In 1957 Hadži organised in Ljubljana the first post-war international conference devoted to hydrogen bondig. Because of the importance of the subject this was an extremely successful meeting attended by distinguished scientists from all over the world. This included individuals of the calibre of L. Pauling and G. Pimentel from USA, J. D. Bernal and C. A. Coulson from the United Kingdom, M. Eigen from Germany, and M. A. Wolkenstein and N. D. Sokolov from the Soviet Union. The experimental spectroscopic phenomena associated with hydrogen bonds, and their possible theoretical interpretations, were discussed at length at the meeting and Hadži's own contributions were very well received. The occasion did much credit to Hadži's own Institute and to the University of Ljubljana, and indeed to Yugoslavian chemistry in general. Shortly before this meeting Hadži and Bratož had published an important theoretical paper. In this they showed how many of the spectroscopic features associated with hydrogen bonds of at least moderate strength could be accounted for in terms of vibrational anharmonicity including the coupling of νXH and νXH . . . X normal modes of vibration. This exposition formed a very relevant background to the discussion of infrared spectra of such systems at the Ljubljana conference.

An important factor in contributing to the success of the studies of hydrogen bonding by Hadži's school, has been that the ideas generated by the interesting infrared phenomena were also thoroughly tested and explored through the use of many other physical methods of determining molecular structure. These included the exploration of far infrared spectra, Raman spectra, solid-state NMR spectra with Blinc, liquid state NMR, dielectric measurements, and the correlation of infrared spectra with X-ray and neutron crystallographic studies with Speakman. The X-ray technique studies very strong hydrogen bonding through the observation of very short X . . . X distances. Also crystallographic symmetry considerations provided criteria for distinguishing between such hydrogen bonds which were symmetrical or which were not. Neutron diffraction provided evidence, not always unambiguous, for the locations of the hydrogen atoms.

Hadži's studies have not been confined to the solid-state where very strong hydrogen bonds are most readily observed. Systematic studies of liquid or solution state mixtures of a particular acidic XH group with organic bases of different strengths also revealed similar strong and broad νXH bands of very low frequency. In some of these cases there was necessarily chemical asymmetry in the hydrogen bond because of different X and Y groups in the X—H . . . Y system. In such cases if two potential minima do occur for hydrogen positions these cannot be of equal depth except by improbable chance. These studies led to a realisation that the double-minimum interpretation of some of the A, B, C spectra could not be of general validity. The same conclusion was drawn from comparisons of infrared and Raman spectra which should, but did not seem to, show bands from different transitions between energy levels in a symmetrical double-minimum situation.

In a plenary review lecture at a IUPAC-sponsored conference in 1965, Hadži renewed the more general anharmonicity interpretation of multiple-band νXH spectra. This involved the possibilities of Fermi resonance of the νXH vibration with overtones of in-plane δXH and out-of-plane γXH modes. With somewhat different emphasis, this idea was supported by work from our own laboratory. In this Claydon and I pointed out that, given the occurrence of an initial very broad νXH absorption, Fermi resonance with δXH or γXH modes could produce minima in the broad continuum, as previously demonstrated by Evans in a different context. In his review paper Hadži also once again drew particular attention to the very broad bands centred in the 1000 cm^{-1} region or below and amphasised that these could be correlated with extremely short X . . . X distances in the crystal structure. Some of these crystal structures could be interpreted in terms of symmetrical and centred hydrogen bonds, and others in terms of quasi or nearly centred systems. Subsequently Hadži and Orel, and also his earlier colleague Novak now working in France, showed that these two cases could be distinguished in the infrared spectra, with the truly centred hydrogen bonds giving much more normal isotopic shifts in going from X . . . H . . . X to X . . . D . . . X.

Another of Hadži's earlier colleagues, Professor S. Bratož, had made a very successful career of his own in France, on the theoretical side. He has shown, within the past few years, how the broad and smooth νXH bands from hydrogen bonded systems in solution can be interpreted in terms of time dependent stochastic treatments of molecular motions giving rise to a range of X . . . X distances that can be present.

It can be concluded that the personal contribution of Dušan Hadži to our understanding of hydrogen bonding has been of major importance. His Ljubljana School has also given initial trainings to a number of highly able spectroscopists and chemical physicists who have made important contributions to this research field both in Ljubljana and elsewhere.

In this account of Professor Hadži's work I have concentrated on his important and coherent contributions to hydrogen bond research. However he has, of course, made many other contributions to the chemical spectroscopic literature. These include infrared structural studies of chemical groupings containing the NH bond, including studies of tautomerism and isomerism, of OH/OD angle deformation modes, peroxybenzoic acids, and Lewis type acid-base complexes. He and his colleagues have also made very effective use of CNDO-type electronic structure calculations and normal-coordinate vibrational analyses in investigating molecular structures in more detail. The Ljubljana school has also shown much interest in the use of computer-based search systems for infrared spectroscopy, or for infrared combined with NMR (^{1}H and ^{13}C) and mass spectral data. These techniques are of great aid in determining the structures of larger molecules and Dušan Hadži's own interests have recently turned to such studies as applied to molecular pharmacology. Since the early 1970's he has also been very active in promoting research programmes with other laboratories on an international basis. Overall he has some 160 research publications to his credit including a number of authoritative review articles in books and elsewhere.

Professor Hadži has spent most of his scientific career in Ljubljana where he was born in 1921. Apart from his period in Cambridge, he also worked at different times with Professor Freyman in Rennes and with Professor Foil Miller in Pittsburgh. He obtained his first degree in chemistry from the University of Ljubljana in 1944. In 1953 he was appointed Lecturer in Theoretical Organic Chemistry, and in 1957 to the Chair of Structural Chemistry, both at the University of Ljubljana. He has for many years been Director of Research at the Institute Boris Kidrič in Ljubljana and has recently been appointed as Science Adviser to the Director-General of Chemical and Pharmaceutical Works — LEK. He has been the recipient of many honours for his scientific work. He is a member of the Slovenian, Serbian and Yugoslav Academy of Sciences and a Foreign Member of the Indian National Academy of Sciences. He was awarded the Boris Kidrič Prize in 1976 and has served as President of the Slovenian Chemical Society. He was awarded the degree of Doctor Honoris Causa of the University of Uppsala, Sweden, in 1980. The international recognition of his work is also reflected in his membership of the Editorial Boards of Spectrochimica Acta, the Journal of Molecular Spectroscopy and Spectroscopy Letters. He is a member of the Royal Chemical Society (London), the Societé de Chimie Physique, the Deutsche Bunsengesellschaft and the International Society of Quantum Biology.

If a capability for scientific research was already in Dušan Hadži's blood he has made full use of his intellectual gifts. However his influence has been even wider than his scientific works because of his friendly and enthusiastic personality. This surely has played a major role in the successful building up of the Ljubljana School and in extending its influence widely in the scientific world. His very fruitful career has been much assisted by his wife Andreja who has had to cope with the many problems of being married to a distinguished and busy man, as well as following her own career. Their son, Sasha, is already well established in a career involving computing and physics, and shares his father's interests in international contacts.

We give our warmest greetings to Dušan Hadži on his sixtieth birthday. We look forward to further important contributions from his scientific laboratory, and to continued friendships for years to come.

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