INTAS Workshop “Complete Spectroscopy of Water”, 20-22 May, 2004, N.Novgorod, Russia

HIGH ACCURACY VARIATIONAL CALCULATIONS OF WATER SPECTRA

OLEG L. POLYANSKY
Institute of Applied Physics, Russian Academy of Sciences,
Uljanov Street 46, Nizhnii Novgorod, Russia 603950

The quest to increase the accuracy of the rotation-vibration energy levels calculations of triatomic molecules using variational methods begun for me about ten years ago when the limitations of the effective Hamiltonian approach became apparent [1]. Within variational calculations all the levels up to dissociation could be calculated and the problem of extrapolation to higher excitations is not encountered in such a dramatic form as it is in effective Hamiltoninans. However, the accuracy of such calculations were and still are significantly worse, than in effective Hamiltonian approach.

We can hardly hope to improve this accuracy to microwave standards, which is typical for effective Hamiltonians, but to achieve 0.02 cm^{-1} becomes a realistic goal. In the talk I will show that this accuracy is enough for all reasonable purposes and could be called "experimental". The reason for quotation marks is easy to explain. We did not reach this "experimental" accuracy yet, but we made significant steps towards it. Ten years ago the accuracy of about 1 cm^{-1} we considered to be a big success in the water energy levels calculations [1]. Now 0.028 cm^{-1} for about 70 percent of of the water energy levels and 0.07 cm^{-1} for virtually all the known data (the fit has been done up to $J=5$) on three water isotopomers is achieved recently. Sergei Shirin will be giving more details of our fitting procedure and results in his talk. We hope to achieve "experimental" 0.02 cm^{-1} in our next stage of efforts to improve the accuracy of water energy levels calculations. What gives us this hope and how we achieved the mentioned results? Extremely accurate *ab initio* calculations reported in [2] has been used as a starting point of the fit. 18 000 energy levels of all water isotopomers were calculated in this paper with the accuracy about 1 cm^{-1} using purely *ab initio* methods without a single adjusted parameter. (Note that this is an accuracy of fitted potential only ten years ago). In order to achieve this accuracy all the imaginable corrections - adiabatic, relativistic and even quantum electrodynamics - has been used to augment our quantum chemical calculations of very accurate Born - Oppenheimer surface. Attila Csaszar will give the details of the quantum chemical methods we used. Since the classic work of David Schwenke an extremely accurate *ab initio* starting point became a must for all the attempts to get high accuracy fitted potential energy surface (PES). But that is only a beginning - further significant efforts are necessary to fit PES to "experimental" accuracy. Some of these efforts are described in the talk.

In the final part of the talk I will present some results of the use of our calculations. In particular the examples of the analysis of the water spectra will be given (Nikolay Zobov will talk about it in details) and the analysis of some qualitative effects in water spectra using variational calculations will be presented.

[1]. O. L. Polyansky, P. Jensen and J. Tennyson, J. Chem. Phys., 101, 7651 (1994).
[2]. O. L. Polyansky, A. G. Csaszar, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke and P. J. Knowles, Science, 299, 539 (2003).