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Spectroscopy of Water

reviewed by Jonathan Tennyson and Attila G. Császár

Scientific questions demand scientific explanations. Our understanding of the greenhouse effect on earth and of the radiation balance on planets raises a number of complex scientific questions. These questions and the answers are often discussed in the public media as if the background knowledge was complete, while this is not the case. Most significantly, many of the questions lead to unexplored or at least underexplored territories of high-resolution molecular spectroscopy. In order to move beyond the state-of-the-art in our understanding of the greenhouse effect and the radiative balance of atmospheres of planets, the way the water molecule absorbs and emits light must be understood all the way from the microwave to the visible and ultraviolet regions. This important challenge led the IUPAC Physical and Biophysical Chemistry Division to sponsor the activities of two task groups: first, "A database of water transitions from experiment and theory," (project 2004-035-1-100) and then, "Intensities and line shapes in high-resolution spectra of water isotopologues from experiment and theory," (project 2011-022-2-100). The two task groups have recently completed their work and reported their results and recommendations [1,2], some of which are reviewed briefly below.

Water vapor is both the major absorber of incoming sunlight in a clear sky and also the dominant greenhouse gas in our atmosphere. As a result, a trace species, isotopically-substituted water, $H_2{}^{18}O$, is already the fifth biggest absorber of sunlight in the Earth's atmosphere.

From the theoretical point of view, water is also an interesting molecule. It is a rather non-rigid system meaning that its vibrational modes can absorb light and be excited by multiple quanta. It is also a light, asymmetric rotor which means that the vibrational bands have a very open structure. The result of this is that strong absorption by water bands is found throughout the infrared and, increasingly weakly, throughout the visible region of the electromagnetic spectrum. Indeed, recent atmospheric studies are focusing on vibration-rotation absorption in the near-ultraviolet which means transitions involving the jumps of 8 or 9 vibrational quanta.

The first task group used a methodology co-developed by the two co-authors to create an information system of refined empirical rotation-vibration energy levels, and hence transition frequencies, for altogether nine water isotopologues. The MARVEL (measured active rotation-vibration energy levels) procedure for doing this was refined significantly during the course of the IUPAC-sponsored research efforts. The resulting MARVEL procedure is both robust and computationally efficient; it is now being applied to a number of other molecules of scientific and practical interest.

The energy levels and the comprehensive sets of transition frequencies generated by the TG for the water isotopologues are being used for a variety of applications. For example, a complete set of lines has been generated for $H_2{}^{18}O$ and $H_2{}^{17}O$ by combining MARVEL-based transition frequencies with transition probabilities computed using high-accuracy, first-principles quantum chemistry. These results are incorporated in the latest edition of the canonical HITRAN database, which is extensively used for atmospheric modeling. The energy levels are also being used to update the so-called steam tables, which tabulate the temperature-dependent thermochemical properties of water.

The second task group was formed to answer the question of how to represent the precise shape of a spectroscopic line observed under high resolution, a property which depends considerably on the environment in which the system is being observed. The so-called Voigt profile, a convolution of the Doppler profile, to represent thermal motions, and a Lorentzian, to model collisional effects, has been widely used. But the Voigt profile is known to be inadequate for precise modeling work, leading, for example, to W-shaped systematic residues in atmospheric water spectra. Going beyond the Voigt profile requires the inclusion of a variety of rather subtle collisional effects. Consideration of these effects has led to the proposal of a whole zoo of different possible models and functional forms to represent the line shape. It was clear that databases and modelers require a clear recommendation of a single beyond-Voigt line profile. The TG-recommended profile, which we named the Hartmann-Tran Profile (HTP), has the advantage that it captures the complex physics involved in collisional line-broadening with a functional form that can easily, and rapidly, be evaluated. Furthermore, the HTP profile reduces to other, simpler profiles including Voigt in the absence of a full parameter set.

The HTP profile is suitable for modeling the line profiles of a range of molecules and is beginning to be used for this purpose. It is expected that the HTP profile will also be useful for a number of other molecules and chemical environments.

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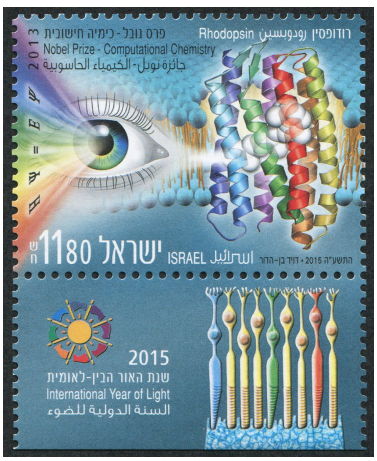
Stamps International



The Chemistry of Vision

The postal authorities of several countries, including Israel, Italy, the Vatican, Bosnia and Herzegovina, Liechtenstein, and Moldova, have recently issued postage stamps to commemorate the International Year of Light and Light-based Technologies (IYL 2015). The colorful stamp released by Israel Post on 27 January, the centerpiece of this note, is not only chock full of symbolism but has particularly strong connections to chemistry.

The top right portion of the stamp features the molecular structure of rhodopsin, a light-sensitive receptor protein that consists of a bundle of seven transmembrane alpha-helices connected by peptide links and a central pocket that binds the chromophore retinal (shown in gray), the photoisomerization of which triggers the process of vision. An open eye, the visible spectrum with the colors of the rainbow, and Schrödinger's equation –every chemist's introduction to quantum mechanics– appear on the stamp to the left of the rhodopsin molecule. The bottom portion of the stamp displays the IYL 2015 logo and a schematic represenatation of the two common photoreceptor cells found in the retina: rods (shown in yellow), which enable vision under low-light conditions, and cones (shown in blue, green, and red), which allow color vision.

Significantly, the stamp also honors Martin Karplus (Harvard University and Université de Strasbourg), Michael Levitt (Stanford University), and Arieh Warshel (University of Southern California), the recipients of the 2013 Nobel Prize in Chemistry "for the development of multiscale models for complex chemical systems". These pioneers of computational biology devised ingenious methods that combined quantum and classical mechanics and allowed the study of a variety of inherently complex processes, including enzymatic and electron transfer reactions, ion transport, and the chemistry of vision. Interestingly, the three scientists closely interacted at various times of their careers and conducted critical aspects of their research at the Weizmann Institute of Technology in Israel. (For biographical sketches of the 2013 Chemistry Nobel laureates, see: J.-M. André, *Chem. Int.* 2014, 36(2), 2-7).

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