The potential energy surface of $H_2{}^{16}O$

Oleg L. Polyansky, *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*; Per Jensen, *FB 9-Theoretische Chemie, Bergische Universität-Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany*; Jonathan Tennyson, *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK.*

We report here a new determination of the $H_2{}^{16}O$ potential energy surface from experimental data. The calculations have been carried out by means of the very accurate and highly efficient method proposed and applied to $H_2{}^{16}O$ in a recent paper[a]. This previous work has been significantly improved by inclusion of additional terms in the analytical expression used to represent the potential energy surface. Previously, 1600 rotation-vibration term values for $H_2{}^{16}O$ were fitted with a standard deviation of 0.36 cm^{-1}. With the extended model of the present work, this standard deviation could be improved to 0.25 cm^{-1}. With the extended model and the new fitted potential function we have calculated a data set comprising 3200 term values, all of which can be compared with experimentally derived values. The standard deviation for this data set is 0.6 cm^{-1}. The data set contains rotationally excited energy levels for all the 63 vibrational states which have been characterized by high resolution spectroscopy. The potential energy function obtained in the present work improves drastically the agreement with experiment for the highly excited local mode stretching states above 20 000 cm^{-1}. For the vibrational band origins of these states, the highest of which is measured at 25 118 cm^{-1}, our previous fitted potential produced discrepancies of more than 100 cm^{-1}. These deviations are reduced to less than 1 cm^{-1} by the potential energy function of the present work. We show that no significant improvement of the fit can be obtained by extending the analytical expression for the potential energy by further high-order terms. An analysis of the residuals shows that at the level of accuracy achieved, the major contribution to the error originates in the neglect of nonadiabatic correction terms in the Born-Oppenheimer kinetic energy operator. We conclude that any further improvement of the potential energy surface requires that such correction terms be included in the Hamiltonian. With the present potential, reliable extrapolations towards higher rotational and vibrational energies can be carried out, and we expect that such calculations can be very helpful in the assignment of experimental spectra involving highly excited states.

[a] O. L. Polyansky, P. Jensen and J. Tennyson, J. Chem. Phys. **101**, 7651 (1994)