Vibrational Calculation of Highly Excited Rovibrational Energy Levels of H_2O_2

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Results are presented for highly accurate *ab initio* variational calculation of the rovibrational energy levels of H_2O_2 in its electronic ground state. These results use a recently computed PES [1] and the variational nuclear-motion programmes WAVR4 [2], which uses an exact kinetic energy operator, and TROVE [3], which uses a numerical expansion for the kinetic energy. The TROVE calculations are performed for levels with high values of rotational excitation, J up to 35. The purely *ab initio* calculations of the rovibrational energy levels reproduce the observed levels with a standard deviation of about 1 cm^{-1}, similar to that of the $J = 0$ calculation as the discrepancy between theory and experiment [4-6] for rotational energies within a given vibrational state is substantially determined by the error in the vibrational band origin. Minor adjustments [7] are made to the *ab initio* equilibrium geometry and to the height of the torsional barrier. Using these and correcting the band origins using the error in $J = 0$ states lowers the standard deviation of the observed − calculated energies to only 0.002 cm^{-1} for levels up to $J = 10$ and 0.02 cm^{-1} for all experimentally know energy levels, which extend up to $J = 35$. Calculations using this slightly adjusted *ab initio* PES results in very smooth variation in the discrepancies between the observed and calculated levels as a function of the rotational quantum numbers J and K_a. It was shown [8] that such smoothness and accuracy is the key to the successful analysis of previously unassignable spectra.

Our ability to probe the molecular composition of extrasolar planets using spectroscopy [9], has led to demand for accurate, comprehensive line lists over an extended range of both temperature and wavelength for all species of possible importance in exoplanet atmospheres [10]. The accuracy of the calculations presented here suggests that the present work will provide an excellent starting point for the calculation of a comprehensive line list for H_2O_2.

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