NEW METHOD OF FITTING EXPERIMENTAL RO-VIBRATIONAL INTENSITIES TO THE DIPOLE MOMENT FUNCTION: APPLICATION TO HCl

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A dipole moment function (DMF) for hydrogen chloride (HCl) has been obtained using a direct fit approach that fits the best available and appropriately weighted experimental data for individual ro-vibrational transitions. Combining wavefunctions derived from an empirical potential and a semi-empirical DMF, line intensities were calculated numerically for bands with Δv=0, 1, 2, 3, 4, 5, 6, 7 up to v'=7. The results have demonstrated the effectiveness of inclusion of rotational dipole moment matrix elements and appropriate weighting of the experimental data in the DMF fitting. The new method is shown to be superior to the common method of fitting only the rotationless dipole moment elements, especially when the experimental data are scarce. While the new approach is more sophisticated it is easy to implement in particular with the use of modern spectroscopic numerical programs, such as Level[a]. We also show that in case the exact potential energy function is not available, the use of wavefunctions derived from the Rydberg-Klein-Rees (RKR) numerical method can be very efficient. Finally, the previously reported dipole moment functions of HCl are critically reviewed.

[a] R. J. Le Roy, "LEVEL 8.0, 2007", University of Waterloo Chemical Physics Research Report CP-663 (2007); see `http://leroy.uwaterloo.ca/programs/`.