An Empirical Potential Energy Surface for the Electronic Ground State of HCO +

Poster · August 2016

DOI: 10.13140/RG.2.2.25736.83200

Per Jensen

Bergische Universität Wuppertal

An Empirical Potential Energy Surface for the Electronic Ground State of HCO^+

Giulia Winterhoff[1], Sarah C. Galleguillos Kempf[1],
Tsuneo Hirano[2], Per Jensen[1]

[1]Bergische Universität Wuppertal, Germany, [2]Ochanomizu University, Tokyo, Japan

Abstract

In a recent publication [1] we reported extensions of the MORBID [2] and RENNER (see Ref. [3] and references therein) programs to refine the potential energy functions of triatomic molecules in simultaneous least-squares fittings of experimentally derived energy differences and *ab initio* energies. In the present work, we employ the extended MORBID program to the electronic ground state of the HCO^+ ion. The experimental data (for HCO^+ and DCO^+) are compiled by Neese [4] and the ab initio energies are newly calculated at the core-valence RCCSD(T)/[aug-cc-pCVQZ(C, O), aug-cc-pVQZ(H)] level of theory. In the fitting of the potential energy surface, we reached a standard deviation of 0.38 cm^{-1} for experimental and *ab initio* data.

Introduction

To simulate molecular spectra we require an analytical, parameterized representation of the potential energy surface (PES) for the particular electronic state of the molecule under study. The PES parameter values can be obtained by least-squares fits of

(1) *ab initio* energies and/or

(2) experimentally derived rovibronic energy spacings.

The experimental data are mostly too limited for the determination of a PES, so we often use Method (1) to determine initial parameter values and then refine these by Method (2). If the experimental information is also too limited for the refinement as in the present case for the electronic ground state of HCO^+, we simultaneously fit the experimental and the ab initio energies with an appropriate weighting of the two data types. The experimental data (for HCO^+ and DCO^+) are collected by Neese [4] and the *ab initio* energies are newly calculated at the RCCSD(T)/[aug-cc-pCVQZ(C,O), aug-cc-pVQZ(H)] level of theory.

Theory

We make the Born-Oppenheimer approximation and so, we solve the Schrödinger equation

$$\hat{H}_{\mathrm{n}}\Psi_{\mathrm{n}} = [\hat{T}_{\mathrm{n}} + (V_{\mathrm{nn}} + V_{\mathrm{elec}})]\Psi_{\mathrm{n}} = E_{\mathrm{ne}}\Psi_{\mathrm{n}}. \tag{1}$$

where $\hat{H}_{\mathrm{n}} = \hat{T}_{\mathrm{n}} + (V_{\mathrm{nn}} + V_{\mathrm{elec}})$ is the nuclear Hamiltonian, Ψ_{n} is the nuclear wavefunction, $\hat{T}_{\mathrm{n}}$ is the nuclear kinetic energy operator, V_{nn} is the Coulombic potential describing the interaction between the nuclei, and V_{elec} is the effective Born-Oppenheimer PES initially determined in the *ab initio* calculation. The quantities E_{ne} are the total, “observable” energies of the molecule. In the MORBID approach, we describe the vibrational motion by three coordinates: r_{j2}, $j = 1$ or 3, is the instantaneous value of the distance between the “outer” nucleus j and the center nucleus 2 and $\bar{\rho}$ is the supplement of the bond angle:

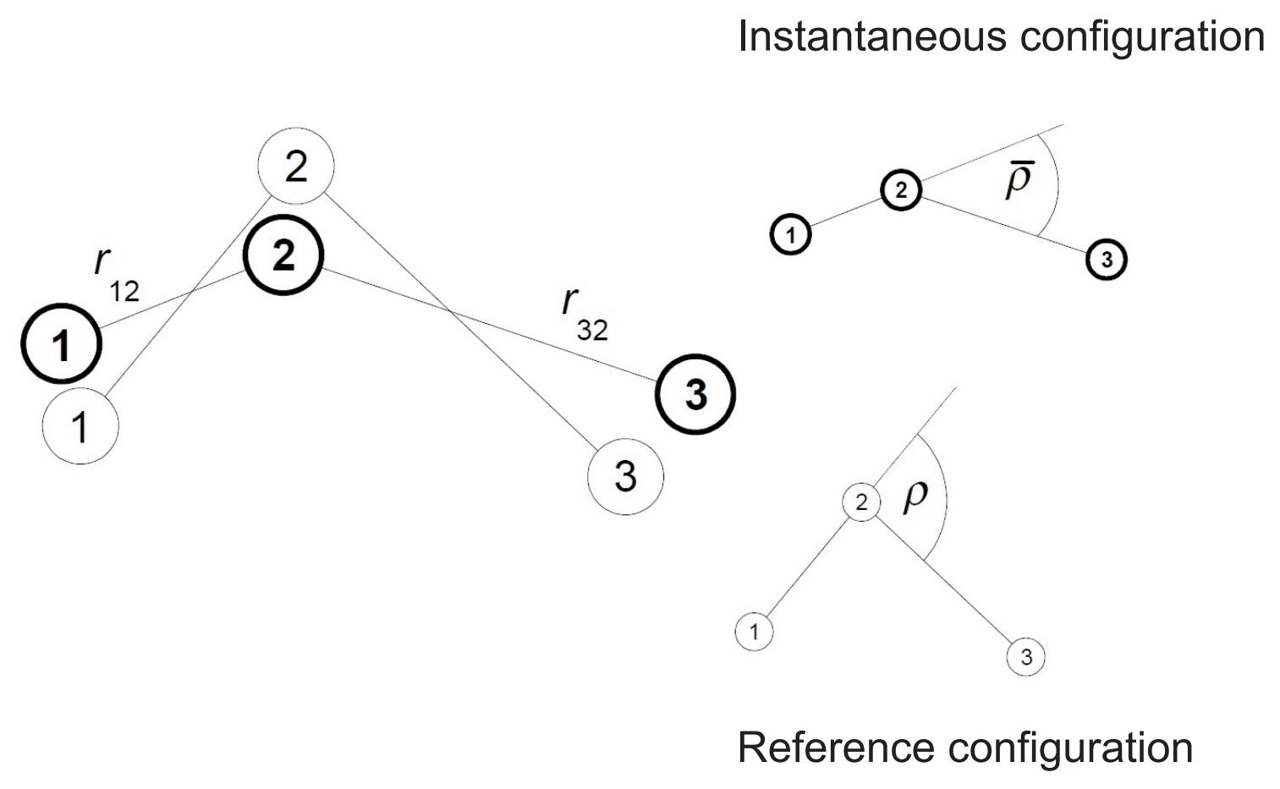

Figure 1: Coordinates used in the MORBID theory.

We label the H, C, and O nuclei as 1, 2, and 3, respectively.

MORBID Calculations

In the calculations of the present work with the extended MORBID program [1, 2], we use the following parameterization of V_{elec}:

$$V_{\mathrm{elec}}(\Delta r_{12}; \Delta r_{32}; \bar{\rho}) = \sum_{jkl} G_{jkl} y_1^j y_3^k (1 - \cos\bar{\rho})^l \tag{2}$$

and

$$y_l = 1 - \exp(-a_l[r_{i2} - r_{j2}^e]), \tag{3}$$

where r_{j2}^e, $j = 1$ or 3, the equilibrium value of r_{j2} and $\Delta r_{j2} = r_{j2} - r_{j2}^e$, the G_{jkl} are expansion coeffcients and, as mentioned above $\bar{\rho} = 180^\circ - \angle$(“molecule”) is the instantaneous value of the molecule bond angle supplement.

Ab initio calculations

The *ab initio* data used as partial input for the least-squares fittings were all computed with the MOLPRO 2010.1 suite of programs [5].

The level of theory employed is core-valence RCCSD(T)/[aug-cc-pCVQZ(C, O), aug-cc-pVQZ(H)].

Least Squares Fitting

The method of least squares is a standard, regression-analysis approach to the approximate solution of overdetermined systems, i.e., sets of equations in which there are more equations than unknowns. ”Least squares” means that the overall solution minimizes the sum of the squares of the errors made in the results of every single equation.

Least squares problems fall into two categories: linear (or ordinary) least squares and non-linear least squares (such as MORBID), depending on whether or not the residuals are linear in all unknowns. The linear least-squares problem occurs in statistical regression analysis; it has a closed-form solution. The non-linear problem is usually solved by iterative refinement; at each iteration the system is approximated by a linear one, and thus the core calculation is similar in both cases.

The best fit in data fitting in the least-squares sense minimizes the sum of squared residuals, a residual being the difference between an observed value and the fitted value provided by a model [6].

Most encountered problems include collinearity in the columns of the model matrix or the lack of experimental data. Attempts to vary too many parameters, and/or lack of information, may lead to difficulties during matrix inversion and unwanted divergence [7].

Refinement of the Potential Energy Surface

For HCO^+, the experimental information available is too limited to allow the determination of a complete PES. One option would be to select a small number of PES parameters and optimize these in a fitting to the small amount of experimental data available. However, there are many possible choices of the parameters to be varied and there is no way of identifying the most suitable one. Also, it is known by experience that fitting to a limited set of experimental data, varying a limited set of parameters, may cause the fitted PES to distort unreasonably in regions of coordinate space not sampled by the experimental data. These problems can be circumvented by the technique employed here, a simultaneous least-squares fittings of experimental and *ab initio* data, in which the two sets of data are weighted appropriately to reflect their different accuracies. The relative weighting must be chosen so as to reflect the fact that experimental measurements are much more accurate than the results of *ab initio* calculations. On the other hand, we generate *ab initio* data points sampling a substantial portion of coordinate space, and these points must be given sufficient weight to prevent the unphysical distortions of the PES.

In the present work, each experimental data point is weighted 100 times higher than an *ab initio* point.

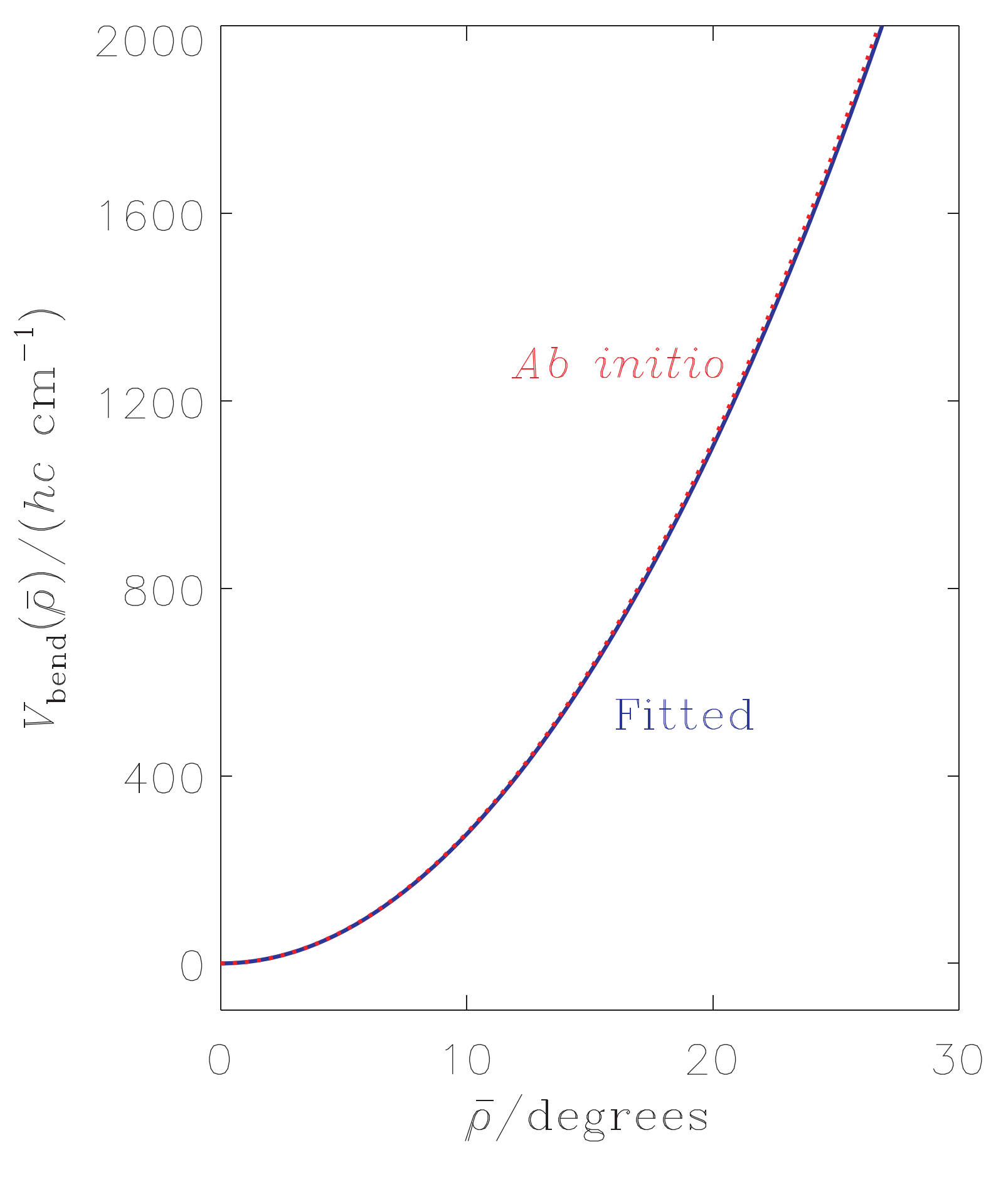

Figure 2: Pure bending potentials for the electronic ground state of HCO^+

Results

Non-zero potential energy parameters (in cm^{-1} unless otherwise indicated) for the electronic ground state of HCO^+

Parameter	*Ab initio*	Fitted	Std. error
G_{001}	18289.2	18148.52	18.863
G_{002}	1652.49	880.2008	314.12
G_{003}	20000.0	23241.37	1504.4
r_{12}^{e}/Å	1.09247	1.099878	0.00039438
r_{32}^{e}/Å	1.10660	1.107158	0.000053628
a_1/$Å^{-1}$	2.6	2.379662	0.0094070
a_3/$Å^{-1}$	1.9	1.9	
G_{101}	−3746.68	−3184.268	237.55
G_{011}	−14851.5	−11573.86	1266.5
G_{012}	0	−85291.16	26618
G_{013}	0	592103.8	165450
G_{110}	20201.6	24168.61	169.00
G_{112}	0	−58850.72	3435.9
G_{020}	153599	153038	97.902
G_{111}	−2185.71	−1782.081	88.092
G_{300}	4980.71	12372.78	288.48
G_{301}	0	−45246.52	4520.1
G_{030}	−38729.7	−32642.18	1132.2

Equilibrium bond lengths for HCO^+ (in Å) compared to results of previous work.

Source	data	r(CH)	r(CO)	Δr(CH)	Δr(CO)
Present work	exp.+*ab initio*	1.099878	1.107158		
Present work	*ab initio*	1.09247	1.1066	0.007408	0.000558
Dore et al.[8]	experimental	1.09204	1.10558	0.007838	0.001578
Woods [9]	experimental	1.097247	1.104738	0.002631	0.002420
Botschwina et al. [10]	exp.+*ab initio*	1.0919	1.1058	0.007978	0.001358
Schmatz et al. [11]	*ab initio*	1.0935	1.1086	0.006378	0.001442
Puzzarini et al. [12]	*ab initio*	1.0919	1.1055	0.007978	0.001658
Martin et al. [13]	*ab initio*	1.0922	1.1055	0.007678	0.001658

Conclusions

For the HCO^+ ion we have been able to refine the potential energy function, improving the agreement between experiment and theory while deteriorating somewhat the agreement with the *ab initio* energies. We have obtained a standard deviation of 0.38 cm^{-1} starting from 6.75 cm^{-1} with the *ab initio*-values of the parameters. The final root-mean-square deviations are 1.23 cm^{-1} for the experimental data points of HCO^+ and 0.06 cm^{-1} for those of DCO^+.

Acknowledgements

This work is supported by the Deutsche Forschungsgemeinschaft (Project JE 144/24-1).

References

[1] Ivo Forsung Chi Mbapeh, Sarah C. Galleguillos Kempf, and Per Jensen. Spectroscopic Potential Energy Surfaces for the $1^2A'$, $2^2A'$, and $1^2A''$ Electronic States of BeOH. *J. Phys. Chem. A*, 119:10112, 2015.

[2] P. Jensen. A New Morse Oscillator-Rigid Bender Internal Dynamics (MORBID) Hamiltonian for Triatomic Molecules. *J. Mol. Spec.*, 128:478, 1988.

[3] Per Jensen, Gerald Osmann, and P. R. Bunker. The Renner Effect. In Per Jensen and P. R. Bunker, editors, *Computational Molecular Spectroscopy*. John Wiley and Sons Ltd., Chichester, 2000.

[4] C. F. Neese. *Laser spectroscopy of molecular cations of astrophysical interest*. PhD thesis, University of Chicago, 2012.

[5] H.J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, and many others. *MOLPRO, version 2010.1, a package of ab initio programs. See http://www.molpro.net.* 2010.

[6] P. Gans. *Data Fitting in the Chemical Sciences (By the Method of Least Squares)*. John Wiley and Sons, Chichester, 1992.

[7] K. Sarka and J. Demaison. Perturbation Theory, Effective Hamiltonians and Force Constants. In Per Jensen and P. R. Bunker, editors, *Computational Molecular Spectroscopy*. John Wiley and Sons, Chichester, 2000.

[8] L. Dore, S. Beninati, C. Puzzarini, and G. Cazzoli. Study of vibrational interactions in $DCO^{\pm}$ by millimeter-wave spectroscopy and determination of the equilibrium structure of the formyl ion. *J. Chem. Phys.*, 118:7857, 2003.

[9] R. C. Woods. Microwave spectroscopy of molecular ions in the laboratory and in space. *Phil. Trans. R. Soc. Lond.*, 324:141, 1988.

[10] P. Botschwina and S. Schmatz. Introduction and applications of *ab initio* methods. In T. Baer, C. Y. Ng, and I. Powis, editors, *The Structure, Energetics and Dynamics of Organic Ions*. John Wiley and Sons Ltd., Chichester, 1996.

[11] M. Mladenović and S. Schmatz. Theoretical study of the rovibrational energy spectrum and the numbers and densities of bound vibrational states for the system HCO^+/HOC^+. *J. Chem. Phys.*, 109:4456, 1998.

[12] C. Puzzarini, R. Tarroni, P. Palmieri, S. Carter, and L. Dore. Accurate ab initio prediction of the equilibrium geometry of $HCO^{\pm}$ and of rovibration energy levels of $DCO^{\pm}$. *Mol. Phys.*, 87:4:879, 1996.

[13] J. M. L. Martin, P. R. Taylor, and T. J. Lee. Accurate ab initio quartic force fields for the ions $HCO^{\pm}$ and $HOC^{\pm}$. *J. Chem. Phys.*, 99 (1):286, 1993.