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

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In the present work we employed 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 RCCSDT(cc-pVQZ(C, O), aug-cc-pVQZ(H)) level of theory. In the fitting of the potential energy surface, we reached a standard deviation of 0.36 cm⁻¹ for experimental and ab initio data.

Introduction

To simulate molecular spectra we require an analytical, parametrized 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 RCCSDT(cc-pVQZ(C, O), aug-cc-pVQZ(H)) level of theory.

Theory

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

\[ \hat{H}_0 \Psi_n = (T_j + V_j + V_a)_E \Psi_n = E_n \Psi_n, \]

where \( \hat{H}_0 = T_j + V_j + V_a \) is the nuclear Hamiltonian, \( \hat{T}_j \) is the nuclear kinetic energy operator, \( \hat{V}_j \) is the Coulombic potential describing the interaction between the nuclei, and \( \hat{V}_a \) is the effective Born-Oppenheimer PES initially determined in the ab initio calculation. The quantities \( E_n \) are the total, “observable” energies of the molecule.

In the MORBID approach, we describe the vibrational motion by three coordinates: \( v_{jkl} \) = 1 or 3, is the instantaneous value of the distance between the “outer” nuclei \( j \) and \( k \), and the center nucleus \( l \) is the supplement of the bond angle:

\[ \text{Instantaneous configuration} \]

\[ \text{Reference configuration} \]

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 \( V_{\text{MORBID}} \):

\[ V_{\text{MORBID}}(\Delta r_{12}, \Delta r_{13}, \Delta r_{23}) = \sum_{jkl} G_{jkl}(1 - \cos \phi_{jkl})^2 \]

where \( \phi_{jkl} = 1 - \cos[\Phi_{jkl} - \phi_{jkl}] \),

\[ \phi_{jkl} = \cos^{-1}(\cos \Phi_{jkl} \cos \Phi_{jkl}) \]

and \( G_{jkl} \) are expansion coefficients and, as mentioned above \( \phi = 10^{-\alpha} \L (\text{“molecule”}) \) is the instantaneous value of the molecular 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 in core-valence RCCSDT/cc-pVQZ(C, O), aug-cc-pVQZ(H) level of theory.

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 problem is similar in both cases.

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

Most encountered problems include collinarity 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 uncontrollably 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 fitting 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.

Results

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Std. error</th>
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</thead>
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<td>0.0019 0.0019</td>
</tr>
<tr>
<td>( \Delta r_{13} )</td>
<td>1.0919 1.0919</td>
<td>0.007978 0.007978</td>
</tr>
<tr>
<td>( \Delta r_{23} )</td>
<td>1.0922 1.0922</td>
<td>0.0019 0.0019</td>
</tr>
</tbody>
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Equilibrium bond lengths for HCO⁺ (in Å) compared to results of previous work.

<table>
<thead>
<tr>
<th>Source</th>
<th>data</th>
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<th>( \Delta r_{13} )</th>
<th>( \Delta r_{23} )</th>
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Conclusions

For the HCO⁺ ion we have been able to refine the potential energy function, improving the agreement between theory and experiment while introducing 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.

Acknowledgements

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