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
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
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EMPIRICAL POTENTIAL ENERGY SURFACES FOR THE ELECTRONIC GROUND STATES OF BeOH, C₃, AND HCO⁺

Theoretische Chemie, Bergische Universität Wuppertal: I. Forsung Chi Mbapeh, S. C. Galleguillos Kempf, I. Keppeler, G. Winterhoff, P. Jensen
 Department of Physics and Astronomy, University College London: R. Diamantopoulou, J. Tennyson, S. N. Yurchenko
 Faculty of Science, Ochanomizu University: T. Hirano



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 or
2. experimentally derived rovibronic energy spacings.

The experimental data are mostly too limited for the determination of a PES, so we normally use Method (1) to determine initial parameter values and then refine these by Method (2). If the experimental information is too limited for the refinement, we simultaneously fit the experimental and the *ab initio* energies with an appropriate weighting of the two data types.

For BeOH/BeOD, experimental data and *ab initio* energies are taken from Mascariotolo *et al.* For HCO⁺, the experimental data are compiled by Neese and the *ab initio* energies are newly calculated at the RCCSD(T)/[aug-cc-pCVQZ(C,O), aug-cc-pVQZ(H)] level of theory. Finally, for C₃ and its isotopologues, the experimental data are compiled from diverse sources and the *ab initio* energies are newly calculated at the CCSD(T)/aug-cc-pVQZ level of theory.

MORBID CALCULATIONS

We are presently applying the extended MORBID program to obtain PESs for the electronic ground states of BeOH/BeOD, HCO⁺ and C₃. In this approach the following analytical expansion for the potential energy function is used:

$$V(\Delta r_{12}; \Delta r_{32}; \bar{\rho}) = \sum_{jkl} G_{jkl} y_1^j y_2^k (\cos \rho_e - \cos \bar{\rho})^l$$

$$y_l = 1 - \exp(-a_l |r_{12} - r_{12}^e|)$$

$\Delta r_{12} = r_{12} - r_{12}^e$, $l = 1$ or 3 are the instantaneous internuclear distance displacements;

r_{12}^e is the equilibrium value of the distance r_{12} between the "outer" nucleus $l = 1$ or 3 and the "center" nucleus 2 ;

the G_{jkl} are expansion coefficients;

$\bar{\rho} = 180^\circ - \angle$ ("molecule") is the instantaneous value of the molecular bond angle supplement; the equilibrium value is ρ_e .

AB INITIO CALCULATIONS

For nearly all systems of chemical interest the exact solution to the nonrelativistic time independent electronic Schrödinger equation cannot be obtained, so one must introduce approximations. One type of approximations are single reference methods like the Hartree-Fock (HR) mean field theory, which are usually only appropriate near the equilibrium structures. Furthermore there are various multi reference methods like the multi-reference configuration interaction (MRCI) expansion. In programs like MOLPRO, various multi reference electron correlation methods are implemented.

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

The levels of theory employed were as follows:

- BeOH: sa-CASSCF-MRCI+Q; see Mascariotolo *et al.*
- HCO⁺: core-valence RCCSD(T)/[aug-cc-pCVQZ(C, O), aug-cc-pVQZ(H)]
- C₃: CCSD(T)/aug-cc-pVQZ

REFINEMENT OF PES

We present here simultaneous fittings of experimental data and *ab initio* energies for the electronic ground states of the three molecules BeOH, HCO⁺, and C₃. The fittings are carried out with an extended version of the MORBID program, developed in the course of the present work. With the PESs refined in this manner, we hope to be able to provide improved predictions of term values not obtained from experiment so far. For all three molecules, the experimental information available is too limited to allow the determination of complete PESs. 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 mentioned above.

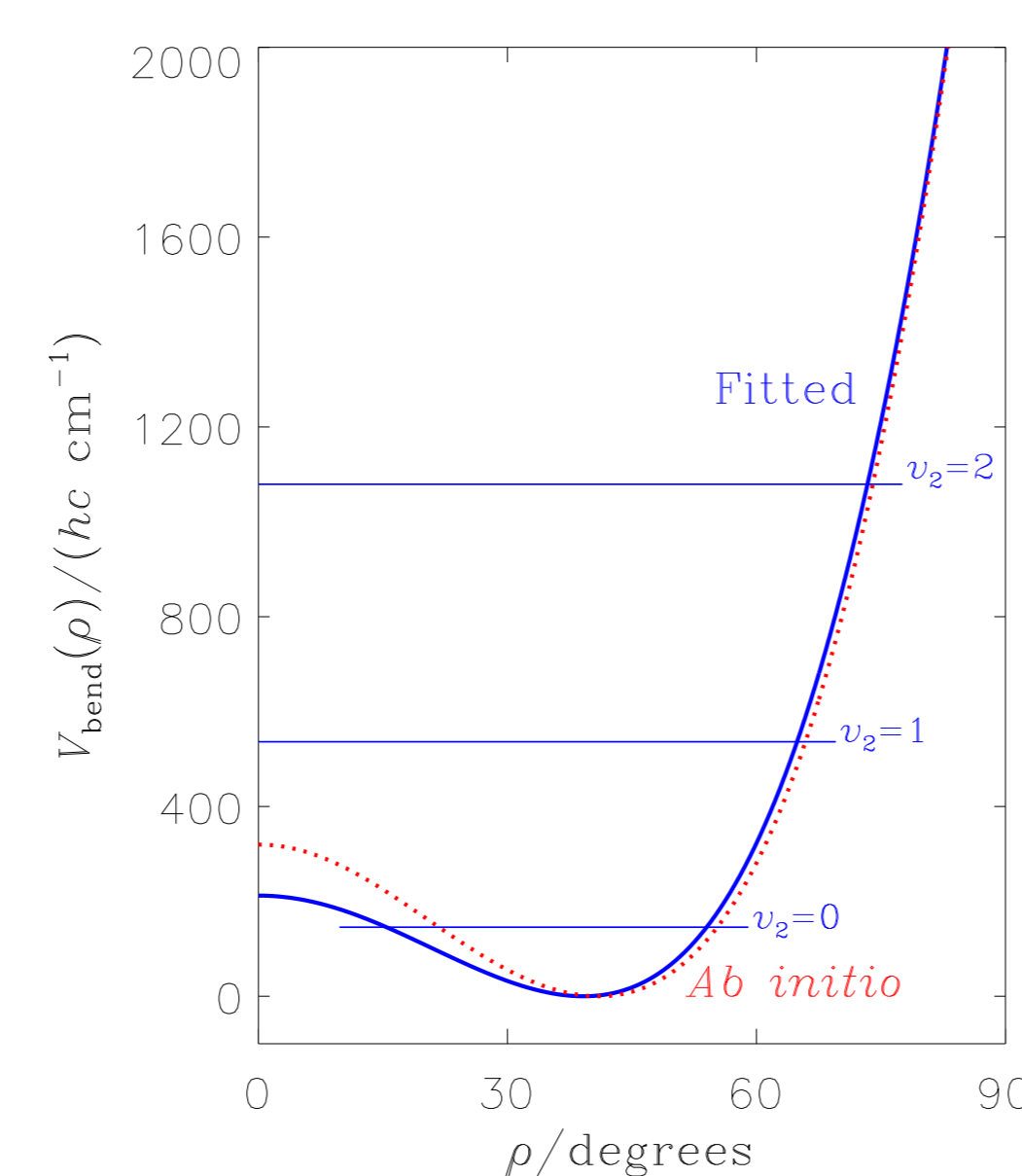
BeOH

Non-zero Potential Energy Parameters (in cm⁻¹ unless otherwise indicated) for the 1²A' Electronic Ground State of BeOH

	Ab initio		Fitted	
	$i = 1$	$i = 3$	$i = 1$	$i = 3$
ρ_e/deg	40.987		39.142(56) ^a	
$r_{12}^e/\text{Å}$	0.943491	1.40148	0.942545(53)	1.399562(88)
$a_i/\text{Å}^{-1}$	2.0	1.7	2.0 ^b	1.7
$f_0^{(2)}$	4230.96		3939(53)	
$f_0^{(3)}$	-1281.47		437.60	
$f_0^{(4)}$	9305.82		4777(224)	
$f_0^{(5)}$	-12945.60		-10141(165)	
$f_0^{(6)}$	6910.56		6910.56	
$f_i^{(1)}$	-5455.87	-13939.10	-5512(54)	-14333(22)
$f_i^{(2)}$	-1415.03	8357.75	-962.73	8421(39)
$f_i^{(4)}$		-2435.08		-2435.08
$f_{ii}^{(0)}$	60101.90	49394.40	60423(92)	49944(55)
$f_{ii}^{(1)}$	-2498.14	1294.51	-2793(27)	559(57)
$f_{ii}^{(2)}$	6252.56	-876.85	-8110.29	257.97
$f_{ii}^{(3)}$		-2106.66		-2349(112)
$f_{iii}^{(0)}$	-5568.37	-3943.47	-9954(285)	-4141(68)
$f_{iii}^{(1)}$		-866.58		83.20
$f_{iiii}^{(0)}$		5441.08		4662(212)

^aQuantities in parentheses are standard errors in units of the last digit given.
^bParameters, for which no standard error is given, were constrained in the final least-squares fitting, either to the *ab initio* value or to a value determined in a preliminary least-squares fitting.

Bending potential energy curves $V_0(\bar{\rho})$ for the electronic ground state 1²A' of BeOH



The two curves are obtained with the 'Ab initio' (red dotted curve) and 'Fitted' (blue solid curve) parameter values from the given table. In obtaining these potential curves, the bond lengths are held fixed at the equilibrium values: $[r(\text{O-H}), r(\text{Be-O})] = [0.943491 \text{ Å}, 1.40148 \text{ Å}]$ for the *ab initio* potential energy function and $[0.942545 \text{ Å}, 1.399562 \text{ Å}]$ for the fitted function. The positions of the three lowest bending energy levels with $K_a = 0$ are indicated for the fitted potential function; only the bending ground state is below the barrier to linearity.

C₃

Non-zero Potential Energy Parameters (in cm⁻¹ unless otherwise indicated) for the Electronic Ground State of C₃

	Former parameters		Fitted parameters		
	Former parameters	Fitted parameters	Former parameters	Fitted parameters	
$r_{12}^e/\text{Å}$	1.29497	1.29804	$f_{13}^{(0)}$	-905.7	-1304.04
$a_1/\text{Å}^{-1}$	2.1	1.92434	$f_{13}^{(1)}$	0.	-1797.04
$f_0^{(1)}$	-55.63	286.999	$f_{13}^{(2)}$	0.	-13739.00
$f_0^{(2)}$	2656.	653.004	$f_{13}^{(3)}$	0.	15230.4
$f_0^{(3)}$	-7390.	-768.773	$f_{11}^{(0)}$	8073.	-1957.78
$f_0^{(4)}$	16270.	1838.80	$f_{11}^{(1)}$	0.	-291.347
$f_0^{(5)}$	-13997.	0.	$f_{11}^{(2)}$	0.	1450.09
$f_0^{(6)}$	5038.	0.	$f_{11}^{(3)}$	0.	-2802.43
$f_1^{(1)}$	-2115.	-1789.79	$f_{113}^{(0)}$	0.	6834.16
$f_1^{(2)}$	-7082.	-1552.56	$f_{113}^{(1)}$	0.	-4827.39
$f_1^{(3)}$	0.	2298.21	$f_{113}^{(2)}$	0.	1324.92
$f_1^{(0)}$	0.	-2163.85	$f_{1111}^{(0)}$	30239.	1324.92
$f_{11}^{(0)}$	57547.	70102.0	$f_{1111}^{(1)}$	0.	2250.52
$f_{11}^{(1)}$	3313.	-2246.36	$f_{1113}^{(0)}$	0.	-2697.98
$f_{11}^{(2)}$	0.	4758.63	$f_{1113}^{(1)}$	0.	1235.88
$f_{11}^{(3)}$	0.	-6518.80	$f_{1133}^{(0)}$	0.	-2896.18
			$f_{1133}^{(1)}$	0.	4808.14

The table shows, as an example, the molecular parameters for the vibrational state (10⁰) for C₃ and the two of its mono ¹³C substituted isotopologues. The column labeled 'Experiment' contains the experimental values fitted by Krieg *et al.*. The next column contains the calculated values from the MORBID program as described by Jensen with the potential energy parameter values given by Špirko *et al.* The right-most column gives the values calculated with the new, preliminary potential energy parameters obtained with the extended version of the MORBID program in the present work.

Effective Parameters (in cm⁻¹) in the Vibrational State (10⁰) of Different Isotopologues of C₃, Obtained by Experiment and by MORBID Calculations

Isotopologue	Parameter	Experiment ^a	MORBID ^b	MORBID ^c
¹² C ¹² C ¹² C	ν	3260.127048(91)	3277.6	3255.22342(17)
	B	0.4241990(25)	0.42423	0.421758(5)
	$D \times 10^6$	1.0760(99)	0.447	1.01(3)
	$H \times 10^9$			1.12(5)
¹² C ¹³ C ¹² C	ν	3205.59319(33)	3221.8	3200.53962(10)
	B	0.424243(27)	0.42418	0.421646(3)
	$D \times 10^6$	1.00(12)	0.812	0.964(17)
	$H \times 10^9$			0.31(3)
¹³ C ¹² C ¹² C	ν	3224.7509(11)	3241.4	3219.959825(4)
	B	0.407586(52)	0.40764	0.4051761(5)
	$D \times 10^6$	0.94(42)	0.270	-0.147(18)
	$H \times 10^9$			-4.3(2)
	$L \times 10^{12}$			12.6(8)

^aParameters: See Krieg *et al.*
^bParameters were determined using the PES of Špirko *et al.*
^cParameters were determined using the PES of the present work.

HCO⁺

Non-zero Potential Energy Parameters (in cm⁻¹ unless otherwise indicated) for the Electronic Ground State of HCO⁺

	Ab initio		Fitted	
	$i = 1$	$i = 3$	$i = 1$	$i = 3$
$r_{12}^e/\text{Å}$	1.09247	1.1066	1.097837	1.107116
$a_i/\text{Å}^{-1}$	2.6	1.9	2.6	1.9
$f_0^{(1)}$	18289.2		18213.847	
$f_0^{(2)}$	1652.49		880.201	
$f_0^{(3)}$	20000		19860.901	
$f_i^{(1)}$	-3746.68	-14851.5	-4208.553	-14309.535
$f_{ii}^{(0)}$	20201.6	153599.	20130.615	153195.807
$f_{ii}^{(1)}$	-1320.33		-2386.206	
$f_{13}^{(0)}$	-2185.71		-2725.335	
$f_{13}^{(1)}$	5503.33		39339.299	
$f_{iii}^{(0)}$	4980.71	-38729.7	8759.705	-31538.32
$f_{113}^{(0)}$	-1633.76		-1633.76	
$f_{iiii}^{(0)}$	0		1589.83	

CONCLUSION AND OUTLOOK

For BeOH/BeOD, the initial, purely *ab initio* predictions allowed a partial but unambiguous assignment of the experimental spectra to be made. We now take the next logical step towards increasing the number of assigned transitions: We use experimentally determined energy spacings to refine the potential energy surfaces for the electronic ground state. The predictions resulting from the refined surfaces are hoped to be more accurate than the original, purely *ab initio* ones so that they will render possible the assignment of additional transitions, involving higher-lying rovibronic energy levels in the electronic ground state.

The band origins for the three isotopologues of C₃ calculated with the preliminary refined PES are now in a better agreement with the experiment than the values obtained with the almost-20-year-old PES of Špirko *et al.* The refinement of the PES for C₃ is still in progress, so this is not the final result. Next steps are to vary more PES parameters to continue reducing the standard deviation and to fit these parameters up to a higher J -level to get, in the future, a better agreement with the experiment and better predictions for band origins.

For the HCO⁺ ion we have been able to improve the errors of the experimental data with the available *ab initio* energies, while at the same time improving the agreement between experiment and theory. The rms deviation for the experimental data of HCO⁺ of 17.622 cm⁻¹ with the initial *ab initio* PES could be improved up to a value of 2.0138 cm⁻¹ because of the refinement of the PESs parameters until now. The weighted standard deviation of the fit was also improved, beginning with 6.1646 cm⁻¹ for the initial *ab initio* PES and ending with 0.85035 cm⁻¹. For the future we hope to further improve the potential energy parameters for HCO⁺ by adding the available experimental data of DCO⁺ to the input data of the fitting.

ACKNOWLEDGEMENTS AND REFERENCES

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