

Potential Energy Surface and Vibrational–Rotational Energy Levels of Hydrogen Peroxide

Jacek Koput*

Department of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland

Stuart Carter

Department of Chemistry, University of Reading, Reading RG6 2AD, U.K.

Nicholas C. Handy

Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, U.K.

Received: February 24, 1998; In Final Form: May 8, 1998

The six-dimensional potential energy surface of hydrogen peroxide, H_2O_2 , has been determined from large-scale ab initio calculations using the coupled-cluster method, CCSD(T), with the basis set of quadruple- ζ quality, cc-pVQZ. The effects of core-electron correlation on the calculated structural parameters and the torsional potential energy function have been investigated. The anharmonic quartic force field has been determined. The vibrational–rotational energy levels of the molecule have then been calculated using the variational method. The calculated molecular properties are found to be in good agreement with experimental data.

1. Introduction

Hydrogen peroxide, H_2O_2 , has recently attracted considerable interest, primarily because the molecule is believed to play an important role in the chemistry of the earth's stratospheric ozone. It is also interesting as one of the simplest molecules performing a large-amplitude motion: internal rotation (torsion) around the OO bond.

The high-resolution spectroscopy of the parent isotopic species, the H_2O_2 molecule, in the gas phase has been the subject of a number of papers (see ref 1 and references therein). On the other hand, the precise experimental data on hydrogen peroxide isotopomers are rather scarce. This is likely why the accurate equilibrium structure and anharmonic force field of the molecule have not been determined to date experimentally. Such a determination of the molecular parameters will be additionally complicated due to the presence of internal rotation and the resulting large anharmonicity effects.

Therefore, state-of-the-art ab initio methods seem to be a valuable alternative for predicting the molecular parameters of hydrogen peroxide. The anharmonic quartic force field of the molecule was determined by two of us² at the self-consistent field (SCF) and second-order Møller–Plesset (MP2) levels of theory. The vibrational energy levels were then calculated by a six-dimensional variational analysis. Harding^{3,4} reported the anharmonic force field determined in configuration interaction calculations with a multireference, generalized valence bond wave function (GVB+1+2). The vibrational energy levels were determined there using a second-order perturbational approach. The equilibrium structure and torsional potential function of the molecule were determined by one of us⁵ at the coupled-cluster level of theory [CCSD(T)].⁶

In this study, we present a more detailed characterization of the potential energy surface and vibrational–rotational energy levels of hydrogen peroxide. The reliable prediction of molecular properties by ab initio methods requires two primary

ingredients: namely, a large one-particle basis set and accurate inclusion of the electron correlation effects. This has been accomplished here by using large polarized basis sets, up to spdfg quality, and by accounting for the valence- and core-electron correlation effects with the coupled-cluster method. The vibrational–rotational energy levels are then calculated by a variational method using an exact representation of the kinetic energy operator.

2. Method of Calculation

The molecular parameters of hydrogen peroxide were calculated using the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).^{7–11} The one-particle basis set employed is the correlation-consistent polarized basis set of quadruple- ζ quality, cc-pVQZ.¹² The cc-pVQZ basis set consists of the (12s6p3d2f1g)/[5s4p3d2f1g] set for oxygen and the (6s3p2d1f)/[4s3p2d1f] set for hydrogen. Only the spherical harmonic components of polarization d to g functions were used. In the correlation treatment involving only the valence electrons, the 1s-like core orbitals of the oxygen atoms were excluded from the active space.

The core-related correlation effects were investigated using the correlation-consistent polarized core–valence basis sets, cc-pCVnZ¹³ and cc-pwCVnZ.¹⁴ The basis sets of triple- ζ quality were employed. The core–valence basis set is obtained by augmenting the standard cc-pVTZ basis set for oxygen with the (2s2p1d) set, and it consists thus of the (12s7p3d1f)/[6s5p3d1f] set for oxygen and the (5s2p1d)/[3s2p1d] set for hydrogen. For both types of the core–valence basis sets, the exponents of the augmenting functions were determined by optimizing the total core–valence correlation energy in the atoms.^{13,14} For the cc-pCVnZ basis set, the core–core and core–valence correlation energies were equally weighted, whereas for the cc-pwCVnZ basis set, the core–valence

correlation energy was heavily weighted over the core–core correlation energy.

The CCSD(T) calculations were performed using the MOL-PRO-96 program.^{15,16}

Vibrational–rotational energy levels of hydrogen peroxide were determined using the variational method. The energy levels were calculated using the nine-dimensional vibration–rotation Hamiltonian of a tetraatomic molecule developed by two of us.^{17,18} The Hamiltonian was derived in terms of the internal coordinates. It consists of an exact representation of the kinetic energy operator and a representation of the potential energy operator in valence curvilinear coordinates. The initial basis set consisted of Morse or harmonic oscillator functions for the stretching coordinates, associated Legendre functions for the bending coordinates, and trigonometric functions sine and cosine for the torsional coordinate. Expansion functions were formed as products of contracted combinations of the initial basis set functions, and the matrix elements were evaluated by numerical quadrature. For each value of the rotational quantum number J , the secular matrix was constructed using the vibrational expansion functions and the rotational symmetric-top functions and then diagonalized to obtain the vibrational–rotational energy levels and wave functions.

The number of the initial stretching functions was 10 for each OH bond stretching coordinate and 15 for the OO bond stretching coordinate. The number of initial bending functions was 21 for each coordinate, and the number of initial torsional functions was 75. The initial functions were contracted in several steps. In the first step, the optimum three-dimensional stretch functions were determined and 25 contracted functions were selected for each symmetry species. In the second step, the optimum torsional functions were determined and 23 contracted functions were selected. In the third step, the optimum two-dimensional bending functions were determined and used together with the optimum torsional functions to construct the optimum three-dimensional bending-torsional functions. Next, 240 functions contracted in this way were selected and used with the optimum stretch functions to construct the final vibrational basis set. For each symmetry species, the final vibrational basis set consisted thus of a total of 6000 contracted functions. This size of the basis set ensured the convergence in the energy to within $\approx 10^{-4}$ cm⁻¹ for the low-lying vibrational–rotational energy levels.

3. Results and Discussion

In the previous study,⁵ the molecular parameters of hydrogen peroxide have been determined by the CCSD(T) method using the correlation-consistent basis sets, ranging from the double- (cc-pVDZ) to quadruple- ζ basis set (cc-pVQZ). With the largest basis set employed, cc-pVQZ, the equilibrium structural parameters were determined to be $r_e(\text{OO}) = 1.4525$ Å, $r_e(\text{OH}) = 0.9627$ Å, $\angle_e(\text{OOH}) = 99.91^\circ$, and $\angle_e(\text{HOOH}) = 112.46^\circ$. The potential energy barriers at the trans and cis conformations of the H₂O₂ molecule were determined to be $V_{\text{trans}} = 377$ cm⁻¹ and $V_{\text{cis}} = 2545$ cm⁻¹. It was shown that the calculated values tend to approach well-defined asymptotic limits with enlargement of the one-particle basis set. With respect to extension of the one-particle basis set beyond cc-pVQZ quality [at the CCSD(T) level of theory], the calculated values of the structural parameters were estimated to be in error by approximately 0.001 Å and 0.1°. The torsional HOOH angle was found to be the most sensitive to extension of the basis set.

In the above-mentioned calculations only correlation of the valence electrons has been taken into account, and therefore in

TABLE 1: Molecular Parameters of Hydrogen Peroxide, Determined Using the CCSD(T) Method and the cc-pCVTZ and cc-pwCVTZ Basis Sets

	valence-only (V) ^a	all-electrons (A) ^b	A – V
cc-pCVTZ			
$r_e(\text{OO})$ (Å)	1.4575	1.4552	–0.0023
$r_e(\text{OH})$ (Å)	0.9637	0.9630	–0.0007
$\angle_e(\text{OOH})$ (deg)	99.57	99.64	0.07
$\angle_e(\text{HOOH})$ (deg)	113.86	113.97	0.11
V_{trans} (cm ⁻¹)	369.5	367.5	–2.0
V_{cis} (cm ⁻¹)	2586	2594	8
cc-pwCVTZ			
$r_e(\text{OO})$ (Å)	1.4575	1.4552	–0.0023
$r_e(\text{OH})$ (Å)	0.9635	0.9628	–0.0007
$\angle_e(\text{OOH})$ (deg)	99.56	99.63	0.07
$\angle_e(\text{HOOH})$ (deg)	113.95	114.09	0.14
V_{trans} (cm ⁻¹)	368.4	365.8	–2.6
V_{cis} (cm ⁻¹)	2586	2594	8

^a Correlating only the valence electrons. ^b Correlating all the electrons.

the present contribution, we have investigated the effect of core-electron correlation on the molecular parameters. A comparison of the values determined in calculations correlating only the valence electrons with those when all the electrons were correlated is given in Table 1. As can be seen, the changes in the molecular parameters (A – V) determined with both of the basis sets, cc-pCVTZ and cc-pwCVTZ, are essentially the same. Inclusion of the core-related correlation effects slightly decreases the OO and OH bond lengths and increases the OOH and HOOH angles.

The best estimate of the equilibrium structural parameters of hydrogen peroxide at the CCSD(T) level of theory can be determined by adding the changes in the parameters due to the core-related correlation effects to the values determined previously with the cc-pVQZ basis set.⁵ In this way, the equilibrium structural parameters are estimated to be $r_e(\text{OO}) = 1.4502$ Å, $r_e(\text{OH}) = 0.9620$ Å, $\angle_e(\text{OOH}) = 99.98^\circ$, and $\angle_e(\text{HOOH}) = 112.58^\circ$. Although the accurate experimental equilibrium structure of hydrogen peroxide has not been determined to date, the calculated values are in good agreement with the crude estimates of the experimental equilibrium structural parameters $r_e(\text{OO}) = 1.452$ Å, $r_e(\text{OH}) = 0.965$ Å, $\angle_e(\text{OOH}) = 100^\circ$, and $\angle_e(\text{HOOH}) = 112^\circ$.⁵ The experimental values were estimated by combining the results reported in refs 19 and 20.

Likewise, the best estimate of the potential energy barriers for internal rotation around the OO bond are calculated to be $V_{\text{trans}} = 375$ cm⁻¹ and $V_{\text{cis}} = 2550$ cm⁻¹. The calculated torsional barriers are close to the experimental values of 385²⁰/387 cm⁻¹²¹ and 2488²⁰/2563 cm⁻¹,²¹ respectively. However, it must be pointed out that the theoretical values of the trans and cis barrier heights are the equilibrium (mass-independent) values, whereas the quoted experimental values are effective only including contributions of the five small-amplitude vibrations of the H₂O₂ molecule. The accuracy of the calculated potential energy parameters can however be appreciated by comparing the calculated vibrational–rotational energy levels to those determined experimentally.

Therefore, the potential energy surface of hydrogen peroxide was determined by calculating the total energy at 281 points in the vicinity of the expected minimum and of the trans and cis conformations. The energies were determined to an accuracy better than 10⁻⁸ hartree and range to approximately 6000 cm⁻¹ above the minimum.

The potential energy surface was then approximated by a six-dimensional expansion along the internal valence coordinates.

The internal coordinates for the stretching modes were chosen as Simons–Parr–Finlan coordinates,²² $q = (r - r_e)/r$, where r and r_e are instantaneous and equilibrium bond lengths, respectively. The coordinate for the OO bond stretching mode is referred to hereafter as q_1 , while those for the OH bond stretching modes as q_2 and q_3 . For the HOO bending modes and the HOOH torsional mode, curvilinear internal coordinates were used,²³ defined by $q = (\angle - \angle_e)(\text{HOO})$ for the bending modes and $q = \angle(\text{HOOH})$, the dihedral angle between the two HOO planes, for the torsional mode. The HOO bending coordinates, adjacent to the q_2 and q_3 coordinates, are referred to hereafter as q_4 and q_5 , respectively. The HOOH torsional coordinate is referred to hereafter as q_6 .

Two different analytic forms for the potential energy surface of hydrogen peroxide have been used. The first form was taken as

$$V(q_1, q_2, q_3, q_4, q_5, q_6) = v_m + V_t(q_6) + V_{\text{sav}}(q_1, q_2, q_3, q_4, q_5, q_6) \quad (1)$$

where v_m is the constant total energy offset, V_t is the potential energy function for the torsional mode, and V_{sav} is the potential energy function for the small-amplitude vibrations, i.e. the stretching and bending modes. The function V_t can be expressed as a trigonometric series of the form

$$V_t(q_6) = v_1 \cos q_6 + v_2 \cos 2q_6 + v_3 \cos 3q_6 + v_4 \cos 4q_6 + \dots \quad (2)$$

The function V_{sav} can be expressed as a polynomial series in the coordinates $\{s_i\} = q_1, q_2, q_3, q_4, q_5$ of the form

$$V_{\text{sav}}(\{s_i\}; q_6) = \sum_{ij} f_{ij} s_i s_j + \sum_{ijk} f_{ijk} s_i s_j s_k + \sum_{ijkl} f_{ijkl} s_i s_j s_k s_l + \dots \quad (3)$$

The equilibrium bond lengths r_e and valence angles \angle_e , as well as the expansion coefficients f (force constants), are assumed here to be functions of the torsional coordinate q_6 . All these parameters can be expressed as trigonometric series of the form

$$p_e = p_e^{(0)} + p_e^{(1)} \cos q_6 + p_e^{(2)} \cos 2q_6 + \dots \quad (4)$$

where p_e is the equilibrium bond length or valence angle, and

$$f_{ij} = f_{ij}^{(0)} + f_{ij}^{(1)} \cos q_6 + f_{ij}^{(2)} \cos 2q_6 + \dots \quad (5)$$

with similar expansions for the other higher-order force constants f . In this way, the potential energy function for the torsional mode, V_t , represents a minimum-energy path along the coordinate q_6 .

The expansion parameters in eqs 1–5 were determined from a least-squares fit of eq 1 to the calculated total energies. In the fit to all 281 data, 90 parameters appeared to be statistically significant. The optimized values of the structural parameters and quadratic force constants are listed in Table 2.²⁴ Only the force constants that are not equivalent by symmetry are quoted. The root-mean-square deviation of the fit was 1.8 μ hartrees (0.4 cm^{-1}).

As can be seen, among the structural parameters the equilibrium OOH valence angle changes the most along the torsional coordinate q_6 , with the difference between the trans and cis conformations amounting to nearly 6°. The equilibrium bond lengths change to much smaller extents, with the OH bond length being nearly constant. The diagonal quadratic force constants appear to be essentially independent of the torsional coordinate q_6 . On the other hand, some of the off-diagonal

TABLE 2: Parameters of the Potential Energy Surface (Eqs 1–5) of Hydrogen Peroxide Determined at the CCSD(T)/cc-pVQZ Level of Theory^a

$r_e^{(0)}(\text{OO})$	1.45625	$f_{11}^{(0)}$	1.0874
$r_e^{(1)}(\text{OO})$	-0.00118	$f_{11}^{(1)}$	-0.0160
$r_e^{(2)}(\text{OO})$	0.00684	$f_{11}^{(2)}$	-0.0116
$r_e^{(3)}(\text{OO})$	0.00068	$f_{22}^{(0)}$	0.8594
$r_e^{(0)}(\text{OH})$	0.96272	$f_{22}^{(1)}$	-0.0107
$r_e^{(1)}(\text{OH})$	0.00090	$f_{22}^{(2)}$	0.0046
$r_e^{(2)}(\text{OH})$	-0.00058	$f_{44}^{(0)}$	0.1111
$r_e^{(3)}(\text{OH})$	-0.00015	$f_{44}^{(1)}$	0.0010
$\angle_e^{(0)}(\text{OOH})$	101.034	$f_{44}^{(2)}$	0.0009
$\angle_e^{(1)}(\text{OOH})$	2.823	$f_{12}^{(0)}$	-0.0380
$\angle_e^{(2)}(\text{OOH})$	0.187	$f_{12}^{(1)}$	-0.0012
$\angle_e^{(3)}(\text{OOH})$	0.089	$f_{12}^{(2)}$	-0.0105
v_m	-151.404524	$f_{14}^{(0)}$	0.1775
v_1	0.0047267	$f_{14}^{(1)}$	-0.0204
v_2	0.0029489	$f_{14}^{(2)}$	-0.0106
v_3	0.0002139	$f_{23}^{(0)}$	-0.0006
v_4	0.0000121	$f_{23}^{(1)}$	-0.0050
		$f_{24}^{(0)}$	0.0007
		$f_{25}^{(0)}$	0.0132
		$f_{45}^{(0)}$	-0.0212
		$f_{45}^{(1)}$	0.0042
		$f_{45}^{(2)}$	

^a The bond lengths are given in angstroms, the angles in degrees, and the expansion coefficients v and f in hartrees.

constants are found to be quite sensitive to changes in the HOOH angle, especially the force constant f_{45} describing interaction between the OOH bending vibrations.

The minimum-energy path along the torsional coordinate q_6 is determined to be

$$V_t(q_6) = 1037.4 \cos q_6 + 647.2 \cos 2q_6 + 46.9 \cos 3q_6 + 2.7 \cos 4q_6 \quad (6)$$

where the expansion coefficients are given in cm^{-1} and the higher-order terms are neglected (the coefficient v_5 is found to be smaller than 0.5 cm^{-1}). The function V_t determined here is nearly identical to that found previously.⁵ It has a minimum at the HOOH dihedral angle of 112.5° and the trans and cis barriers to internal rotation of 377 and 2545 cm^{-1} , respectively.

Since the form for the potential energy surface given by eq 1 could not be used directly in variational calculations of the vibrational–rotational energy levels of hydrogen peroxide, another form was taken as

$$V(q_1, q_2, q_3, q_4, q_5, q_6) = \sum_{ijklmn} c_{ijklmn} q_1^i q_2^j q_3^k q_4^l q_5^m \cos nq_6 \quad (7)$$

The expansion given above involves, in general, linear terms in the small-amplitude coordinates $\{s_i\}$, such as, for example, $q_i \cos nq_6$. Therefore, the coordinates $\{s_i\}$ are defined here with respect to some constant bond lengths r_m and valence angles \angle_m , which obviously are different from the equilibrium values r_e and \angle_e , respectively.

In the least-squares fit of eq 7 to the same set of 281 data as previously, 92 parameters appeared to be statistically significant. The optimized values of the parameters, which are not equivalent by symmetry, are listed in Table 3. The root-mean-square deviation of the fit was 1.4 μ hartrees (0.3 cm^{-1}).

The calculated potential energy surface was modified to account for changes in the structural parameters and in the torsional potential function due to the core-related correlation effects. The corrections (A – V) given in Table 1 were added

TABLE 3: Parameters of the Potential Energy Surface (Eq 7) of Hydrogen Peroxide Determined at the CCSD(T)/cc-pVQZ Level of Theory^a

<i>i j k l m n</i>	<i>c</i>	<i>i j k l m n</i>	<i>c</i>
0 0 0 0 0 0	-151.404 224 61	0 1 0 3 0 0	0.030 578 88
0 0 0 0 0 1	0.004 824 09	0 3 0 1 0 0	-0.063 639 99
0 0 0 0 0 2	0.003 251 27	0 0 0 1 3 0	-0.003 739 64
0 0 0 0 0 3	0.000 266 30	2 1 1 0 0 0	-0.041 146 68
0 0 0 0 0 4	0.000 041 35	2 1 0 1 0 0	0.112 496 14
2 0 0 0 0 0	1.081 549 98	2 1 0 0 1 0	0.026 166 79
0 2 0 0 0 0	0.860 977 23	2 0 0 1 1 0	-0.078 244 25
0 0 0 2 0 0	0.110 161 12	1 1 0 2 0 0	0.042 662 05
1 1 0 0 0 0	-0.036 377 40	1 2 0 1 0 0	-0.074 204 32
1 0 0 1 0 0	0.174 918 54	1 2 0 0 1 0	-0.082 512 68
0 1 1 0 0 0	0.000 570 54	1 0 0 1 2 0	0.002 709 40
0 1 0 1 0 0	-0.001 379 67	0 1 1 2 0 0	0.001 999 53
0 1 0 0 1 0	0.000 621 52	0 2 0 1 1 0	-0.012 923 25
0 0 0 1 1 0	0.013 757 26	0 1 0 1 2 0	-0.020 743 23
3 0 0 0 0 0	-1.156 914 21	0 1 0 2 1 0	-0.007 897 32
0 3 0 0 0 0	-0.254 959 18	1 0 0 0 0 1	-0.014 353 26
0 0 0 3 0 0	-0.022 728 30	0 1 0 0 0 1	-0.001 807 10
2 1 0 0 0 0	-0.183 814 15	0 0 0 1 0 1	-0.011 356 71
2 0 0 1 0 0	-0.346 272 37	2 0 0 0 0 1	0.000 206 55
1 2 0 0 0 0	0.139 745 88	0 2 0 0 0 1	-0.004 925 33
1 0 0 2 0 0	-0.272 904 55	0 0 0 2 0 1	0.002 709 90
0 1 2 0 0 0	-0.006 747 21	1 1 0 0 0 1	0.003 760 86
0 1 0 2 0 0	-0.021 795 45	1 0 0 1 0 1	0.000 447 32
0 2 0 1 0 0	-0.021 256 43	0 1 1 0 0 1	0.005 699 79
0 1 0 0 2 0	-0.004 919 68	0 1 0 1 0 1	-0.002 447 74
0 2 0 0 1 0	0.002 337 73	0 0 0 1 1 1	-0.020 655 64
0 0 0 1 2 0	-0.000 500 66	3 0 0 0 0 1	0.052 493 31
1 1 1 0 0 0	0.018 175 36	0 3 0 0 0 1	-0.024 902 99
1 1 0 1 0 0	-0.046 660 09	0 0 0 3 0 1	0.003 914 60
1 1 0 0 1 0	-0.024 247 48	1 2 0 0 0 1	0.088 937 44
1 0 0 1 1 0	-0.017 271 48	1 0 0 0 0 2	-0.010 516 18
0 1 1 1 0 0	-0.004 205 06	0 1 0 0 0 2	0.001 204 79
0 1 0 1 1 0	-0.006 479 44	0 0 0 1 0 2	-0.001 118 88
4 0 0 0 0 0	-1.067 490 07	2 0 0 0 0 2	0.008 847 57
0 4 0 0 0 0	-0.357 410 07	0 2 0 0 0 2	0.004 162 89
0 0 0 4 0 0	-0.007 968 36	0 0 0 2 0 2	0.001 267 63
2 2 0 0 0 0	-0.425 567 42	1 1 0 0 0 2	-0.007 065 63
2 0 0 2 0 0	0.062 788 96	1 0 0 1 0 2	-0.008 401 46
0 2 0 2 0 0	-0.040 104 19	0 1 1 0 0 2	-0.001 392 19
0 0 0 2 2 0	-0.009 939 12	0 1 0 1 0 2	0.008 016 73
3 1 0 0 0 0	0.475 628 94	0 0 0 1 1 2	0.004 638 60
3 0 0 1 0 0	-0.408 306 27	1 0 0 0 0 3	-0.000 960 51
1 3 0 0 0 0	0.220 732 22	0 1 0 0 0 3	0.000 199 06
1 0 0 3 0 0	0.078 282 12	0 0 0 1 0 3	-0.000 575 76
0 1 3 0 0 0	-0.029 546 87		

^a The expansion coefficients *c* are given in hartrees, determined with $r_m(\text{OO}) = 1.456 199 \text{ \AA}$, $r_m(\text{OH}) = 0.962 755 \text{ \AA}$, and $\angle_m(\text{OOH}) = 100.9059^\circ$.

to the appropriate parameters. The corrections to the parameters ν_1 , ν_2 , and ν_3 (eq 2) were calculated to be +22.6, +3.1, and +0.2 $\mu\text{hartrees}$, respectively. Both unmodified and modified potential energy surfaces were then used to determine the vibrational-rotational energy levels.

The accuracy of the calculated potential energy surface of hydrogen peroxide can be appreciated by comparing the calculated and experimental vibrational-rotational energy levels. For the fundamental frequencies of the small-amplitude vibrations of the H_2O_2 molecule, such a comparison is presented in Table 4. As can be seen, the calculated frequencies are overestimated, with the largest difference between the calculated and observed values being approximately 15 cm^{-1} . Upon inclusion of the core-related correlation effects, the fundamental wavenumbers increase by $1\text{--}3 \text{ cm}^{-1}$. The largest errors are for the stretching modes. The frequencies of both symmetric ν_1 and asymmetric ν_5 OH stretching fundamentals are overestimated by about 15 cm^{-1} , while the frequency of the OO stretching mode ν_3 differs by about $+9 \text{ cm}^{-1}$ from the

TABLE 4: Calculated and Observed Fundamental Wavenumbers (in cm^{-1}) of the Small-Amplitude Vibrations for the H_2O_2 Molecule

mode	calc ^a		obs
	V	C	
ν_1	3624.3	3627.2	3609.80 ^b
ν_2	1396.9	1398.4	1395.88 ^c
ν_3	874.4	875.7	865.94 ^d
ν_5	3625.1	3627.9	3610.66 ^e
ν_6	1267.8	1268.4	1264.58 ^c

^a Determined without (V) and with (C) corrections to the structural parameters and to the torsional potential function due to the core-related correlation effects. ^b Ref 25. ^c Ref 26. ^d Ref 27. ^e Ref 28.

TABLE 5: $J = 0$ Calculated and Observed Energy Levels of Torsional Motion, ν_4 , (in cm^{-1}) for the Ground Vibrational State of the H_2O_2 Molecule

<i>n, τ</i>	calc ^a		obs ^b
	V	C	
0, 1	0.00	0.00	0.00
0, 4	9.91	10.14	11.44
1, 1	261.21	260.87	254.55
1, 4	371.63	372.42	370.89
2, 1	571.12	572.33	569.74
2, 4	776.15	778.14	776.11
3, 1	1000.80	1003.45	1000.88
3, 4	1229.19	1232.20	1235.00

^a Determined without (V) and with (C) corrections to the structural parameters and to the torsional potential function due to the core-related correlation effects. ^b Ref 21.

experimental value. The frequencies of both symmetric ν_2 and asymmetric ν_6 OOH bending fundamentals are overestimated to a smaller extent, by only about 3 cm^{-1} . The energy levels of the torsional motion, ν_4 , are given in Table 5. The energy levels are labeled by two quantum numbers, *n* and τ . The quantum number *n* labels consecutive torsional states, while τ (from 1 to 4) labels the torsional components of a given state in order of ascending energy.²⁹ For the low-lying states, the pairs of torsional components with $\tau = 1$ and 2 or $\tau = 3$ and 4 are degenerate to within experimental accuracy. The observed torsional energy levels are reproduced better than the fundamental frequencies of the small-amplitude vibrations, with the differences between the calculated and observed values being $1\text{--}6 \text{ cm}^{-1}$. Inclusion of the core-related correlation effects results in a small improvement for some of the energy levels; however, it deteriorates the agreement with the experimental data for the others.

Table 6 illustrates calculated and observed torsional energy levels for the first excited states of the small-amplitude vibrations of the H_2O_2 molecule. As seen in the table, differences between the calculated and observed torsional energy levels are similar to those determined for the ground vibrational state. Changes in the torsional energy levels due to excitation of the small-amplitude vibrations are reproduced to better than 5 cm^{-1} . It must be pointed out that the experimental data for the symmetric vibrational modes ν_1 ²⁵ and ν_2 ²⁶ are rather uncertain, with the error bars for some band origins being as large as $4\text{--}12 \text{ cm}^{-1}$.²⁶ The largest changes in the torsional energy levels are observed for excitation of the OOH bending modes ν_2 and ν_6 . This could have been expected given the above-mentioned dependence of the equilibrium OOH valence angle and of the OOH bend/OOH bend interaction force constant f_{45} on the torsional coordinate q_6 . The dependence of the structural parameters and of the harmonic vibrational frequencies on the torsional HOOH angle was discussed in detail by Harding.³ The pattern of the torsional

TABLE 6: $J = 0$ Calculated and Observed Energy Levels of Torsional Motion, ν_4 , (in cm⁻¹) for the First Excited States of the Small-Amplitude Vibrations of the H₂O₂ Molecule

n, τ	calc ^a		obs ^b
	V	C	
ν_1			
0, 1	0.00	0.00	0.00
0, 4	7.13	7.24	8.15
1, 1	266.95	266.37	
1, 4	364.28	365.04	
ν_2			
0, 1	0.00	0.00	0.00
0, 4	5.58	5.71	2.44
1, 1	292.85	292.38	285.17
1, 4	377.62	378.27	373.87
ν_3			
0, 1	0.00	0.00	0.00
0, 4	10.55	10.78	11.99
1, 1	259.56	259.24	251.55
1, 4	376.77	377.88	
ν_5			
0, 1	0.00	0.00	0.00
0, 4	6.95	7.11	8.18
1, 1	273.61	273.16	265.11
1, 4	368.44	369.09	366.42
2, 1	566.31	567.30	563.07
2, 4	763.67	765.46	761.95
ν_6			
0, 1	0.00	0.00	0.00
0, 4	19.32	19.71	20.54
1, 1	241.38	241.40	240.28
1, 4	382.53	383.65	383.78
2, 1	587.72	589.42	589.05
2, 4	806.08	808.51	807.86

^a Relative to the corresponding $(n, \tau) = (0, 1)$ energy level. Determined without (V) and with (C) corrections to the structural parameters and to the torsional potential function due to the core-related correlation effects. ^b ν_1 ref 25, ν_2 ref 26, ν_3 ref 27, ν_5 ref 28, ν_6 ref 26.

energy levels reflects changes in the shape of the effective torsional potential energy function with excitation of the small-amplitude vibrations. In particular, changes in the splittings between the $(n, \tau) = (n, 4)$ and $(n, 1)$ energy levels reflect changes in the height of the effective trans barrier to internal rotation. As can be seen, excitation of the symmetric OOH bending mode ν_2 as well as of both the OH stretching modes ν_1 and ν_5 increases the height of the trans barrier. Upon excitation of the asymmetric OOH bending mode ν_6 , the height of the trans barrier decreases, whereas it remains almost unchanged upon excitation of the OO stretching mode ν_3 . In fact, using an effective one-dimensional torsional Hamiltonian, the trans barrier was determined from the experimental data to be 429 cm⁻¹ in the $\nu_5 = 1$ vibrational state²⁸ and 312 cm⁻¹ in the $\nu_6 = 1$ vibrational state.³⁰

The calculated and observed low- J rotational energy levels of the ground torsional-vibrational state for the H₂O₂ molecule are listed in Table 7. As can be seen, the observed energy levels are reproduced in three figures. The energy levels calculated with the molecular parameters determined correlating only the valence electrons are all systematically underestimated. On the other hand, upon inclusion of corrections due to the core-related correlation effects, the calculated rotational energy levels become all systematically overestimated, resulting in slightly worse agreement with the experimental data. The "true" equilibrium structural parameters of hydrogen peroxide appear thus to lie somewhere midway between the uncorrected and corrected values discussed at the beginning of this section, with the error bars being about one-half corrections due to the core-

TABLE 7: $J = 0-2$ Calculated and Observed Rotational Energy Levels^a of the Four Components of the Ground Torsional-Vibrational State (in cm⁻¹) for the H₂O₂ Molecule

$J_{K_a K_c}$	calc ^b		obs ^c
	V	C	
	$n = 0, \tau = 1, 2$		
0 ₀₀	0.0000	0.0000	0.0000
1 ₀₁	1.7105	1.7152	1.7115
1 ₁₁	10.8983	10.9228	10.9072
1 ₁₀	10.9328	10.9576	10.9426
2 ₀₂	5.1312	5.1453	5.1344
2 ₁₂	14.2845	14.3181	14.2942
2 ₁₁	14.3879	14.4224	14.4019
2 ₂₁	41.9446	42.0384	41.9813
2 ₂₀	41.9447	42.0385	41.9814
	$n = 0, \tau = 3, 4$		
0 ₀₀	0.0000	0.0000	0.0000
1 ₀₁	1.7115	1.7162	1.7128
1 ₁₁	10.8945	10.9188	10.9007
1 ₁₀	10.9252	10.9497	10.9309
2 ₀₂	5.1343	5.1485	5.1375
2 ₁₂	14.2865	14.3200	14.2935
2 ₁₁	14.3784	14.4127	14.3874
2 ₂₁	41.9132	42.0062	41.9447
2 ₂₀	41.9133	42.0063	41.9447

^a Relative to the corresponding $J = 0$ energy level. ^b Determined without (V) and with (C) corrections to the structural parameters and to the torsional potential function due to the core-related correlation effects. ^c Ref 31.

related correlation effects (Table 1). Therefore, these are likely the most accurate values to date for the equilibrium structural parameters of hydrogen peroxide.

The $J = 1$ energy levels allow one to roughly estimate values of the effective, zero-point averaged rotational constants of the H₂O₂ molecule. The energy of the $J_{K_a K_c} = 1_{01}$ rotational level is determined largely by the sum of the effective constants ($B_v + C_v$). For the $n = 0, \tau = 1, 2$ states, the value of ($B_v + C_v$) is calculated to be about 1.7128 cm⁻¹ as compared with the experimental value of 1.7116 cm⁻¹.³¹ For the $n = 0, \tau = 3, 4$ states, the corresponding values are about 1.7138 and 1.7126 cm⁻¹,³¹ respectively. The mean energy of the 1₁₁ and 1₁₀ rotational levels is determined largely by the sum of the effective constants [$A_v + (1/2)(B_v + C_v)$]. For the $n = 0, \tau = 1, 2$ states, the value of [$A_v + (1/2)(B_v + C_v)$] is calculated to be about 10.9279 cm⁻¹ as compared with the experimental value of 10.9252 cm⁻¹.³¹ For the $n = 0, \tau = 3, 4$ states, the corresponding values are about 10.9221 and 10.9161 cm⁻¹,³¹ respectively. On the other hand, the splitting of the 1₁₁ and 1₁₀ rotational levels is determined largely by the difference of the effective constants ($B_v - C_v$). For the $n = 0, \tau = 1, 2$ states, the value of ($B_v - C_v$) is calculated to be about 0.0347 cm⁻¹ as compared with the experimental value of 0.0358 cm⁻¹.³¹ For the $n = 0, \tau = 3, 4$ states, the corresponding values are about 0.0308 and 0.0315 cm⁻¹,³¹ respectively.

Acknowledgment. One of us (J.K.) thanks K. A. Peterson and T. H. Dunning, Jr., for providing the results of their studies prior to publication. This work has been supported by the European Community under the contract CHRXCT 930157 and the associated contract CIPDCT 940614. S.C. wishes to acknowledge support from the U.S. Office of Naval Research Grant N00014-95-1-0493/P00002. Calculations were performed at the Adam Mickiewicz University Poznań and the Technical University Darmstadt.

References and Notes

- (1) Perrin, A.; Flaud, J.-M.; Camy-Peyret, C.; Schermaul, R.; Winnewisser, M.; Mandin, J.-Y.; Dana, V.; Badaoui, M.; Koput, J. *J. Mol. Spectrosc.* **1996**, *176*, 287.
- (2) Willetts, A.; Gaw, J. F.; Handy, N. C.; Carter, S. *J. Mol. Spectrosc.* **1989**, *135*, 370.
- (3) Harding, L. B. *J. Phys. Chem.* **1989**, *93*, 8004.
- (4) Harding, L. B. *J. Phys. Chem.* **1991**, *95*, 8853.
- (5) Koput, J. *Chem. Phys. Lett.* **1995**, *236*, 516.
- (6) A number of papers dealing with the ab initio calculations on hydrogen peroxide, at the lower levels of theory, is further referred to in refs 2–5.
- (7) Čížek, J. *J. Chem. Phys.* **1966**, *45*, 4256.
- (8) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
- (9) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- (10) Scuseria, G. E.; Lee, T. J. *J. Chem. Phys.* **1990**, *93*, 5851.
- (11) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publisher: Dordrecht, 1995.
- (12) Dunning, Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- (13) Woon, D. E.; Dunning, Jr., T. H. *J. Chem. Phys.* **1995**, *103*, 4572.
- (14) Peterson, K. A. Private communication.
- (15) MOLPRO-96 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, R. Lindh, M. E. Mura, and T. Thorsteinsson.
- (16) Hampel, C.; Peterson, K. A.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1.
- (17) Carter, S.; Handy, N. C.; Demaison, J. *Mol. Phys.* **1997**, *90*, 729.
- (18) Bramley, M. J.; Carter, S.; Handy, N. C.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *157*, 301.
- (19) Khachkuruzov, G. A.; Przhhevskii, I. N. *Opt. Spectrosc.* **1974**, *36*, 172.
- (20) Koput, J. *J. Mol. Spectrosc.* **1986**, *115*, 438.
- (21) Flaud, J.-M.; Camy-Peyret, C.; Johns, J. W. C.; Carli, B. *J. Chem. Phys.* **1989**, *91*, 1504.
- (22) Simons, G.; Parr, R. G.; Finlan, J. M. *J. Chem. Phys.* **1973**, *59*, 3229.
- (23) Hoy, A. R.; Mills, I. M.; Strey, G. *Mol. Phys.* **1972**, *24*, 1265.
- (24) The higher-order force constants are available on request from one of us (J.K.).
- (25) Olson, W. B.; Hunt, R. H.; Young, B. W.; Maki, A. G.; Brault, J. W. *J. Mol. Spectrosc.* **1988**, *127*, 12.
- (26) Perrin, A.; Valentin, A.; Flaud, J.-M.; Camy-Peyret, C.; Schriver, L.; Schriver, A.; Arcas, Ph. *J. Mol. Spectrosc.* **1995**, *171*, 358.
- (27) Camy-Peyret, C.; Flaud, J.-M.; Johns, J. W. C.; Noël, M. *J. Mol. Spectrosc.* **1992**, *155*, 84.
- (28) Cook, W. B.; Hunt, R. H.; Shelton, W. N.; Flaherty, F. A. *J. Mol. Spectrosc.* **1995**, *171*, 91.
- (29) Hunt, R. H.; Leacock, R. A.; Peters, C. W.; Hecht, K. T. *J. Chem. Phys.* **1965**, *42*, 1931.
- (30) Perrin, A.; Flaud, J.-M.; Camy-Peyret, C.; Goldman, A.; Murcay, F. J.; Blatherwick, R. D. *J. Mol. Spectrosc.* **1990**, *142*, 129.
- (31) Masset, F.; Lechuga-Fossat, L.; Flaud, J.-M.; Camy-Peyret, C.; Johns, J. W. C.; Carli, B.; Carlotti, M.; Fusina, L.; Trombetti, A. *J. Phys. France* **1988**, *49*, 1901.