ISSN 0030-400X, Optics and Spectroscopy, 2011, Vol. 110, No. 2, pp. 160–166. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © I.I. Bubukina, N.F. Zobov, O.L. Polyansky, S.V. Shirin, S.N. Yurchenko, 2011, published in Optika i Spektroskopiya, 2011, Vol. 110, No. 2, pp. 186–193.

SPECTROSCOPY OF ATOMS AND MOLECULES

Optimized Semiempirical Potential Energy Surface for $H_2{}^{16}O$ up to 26000 cm^{-1}

I. I. Bubukina[a], **N. F. Zobov**[a], **O. L. Polyansky**[a], **S. V. Shirin**[a], **and S. N. Yurchenko**[b]
[a] *Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, 603950 Russia*
[b] *Technische Universität Dresden, Dresden, D-01062 Germany*

Received July 21, 2010

Abstract—A semiempirical potential energy surface is obtained for the major isotopologue of the water molecule $H_2{}^{16}O$ that allows the vibration–rotation energy levels in the range of 0–26000 cm^{-1} to be calculated with an accuracy almost equal to the average experimental accuracy of measurements in the infrared and visible ranges. Variational calculations using this potential energy surface reproduce the experimental energy values of more than 1500 vibration–rotation levels of $H_2{}^{16}O$ with the total angular momentum quantum number $J = 0$, 2, and 5 in the indicated range with a standard deviation of 0.022 cm^{-1}. The potential was obtained by optimizing a starting ab initio surface using a combination of two approaches, i.e., (1) the multiplication of the starting ab initio surface by a morphing function whose parameters were optimized and (2) the optimization of parameters of the ab initio surface using both the experimental values of energy levels and the results of quantum-chemical electronic structure calculations.

DOI: 10.1134/S0030400X11020032

INTRODUCTION

In molecular spectroscopy, the potential energy surface (PES) is an important element in describing and understanding many effects. In a particular electronic state, the PES governs the nuclear motion and, consequently, the vibration–rotation spectrum of this state. At present, the variational calculations are regularly used to determine the semiempirical (effective) PESs for tri- and tetra-atomic molecules [1–5]. Using these surfaces, the energy levels and the wave functions can be obtained in the energy range where the surfaces are correct. Calculations of the energy levels, centers of absorption, and emission lines allow one to assign the spectra and to calculate the theoretical linelists [6]. These linelists are widely used for diverse purposes, e.g., to model the absorption spectra of planets and stars [7]. These applications determine the need to increase the accuracy of calculations of the vibration–rotation spectra of the water molecule and, consequently, its PES. However, the accuracy of variational calculations strongly depends on the quality (smoothness, accuracy, asymptotic behavior) of a PES. Using an ab initio potential as the starting surface, the semiempirical PES is determined using a fitting (optimization) procedure with respect to a relatively small number of parameters. The number of parameters used in the optimization of the potential is significantly smaller than the number of parameters necessary to describe the spectrum using the more traditional method of effective Hamiltonians.

The water molecule is one of the most important triatomic molecules. Therefore, it is no surprise that a large number of semiempirical PESs were obtained for this system [8–15]. The accuracy of calculations using different PESs is constantly improved with time. The improvement of semiempirical PESs is closely connected with the improvement of a starting point in the optimization procedure, which is usually chosen to be a PES from high-precision ab initio electronic structure calculations.

In this paper, a PES was constructed for the major isotopologue of the water molecule that allows us to calculate spectroscopic data in the energy range up to 26000 cm^{-1} with an almost experimental accuracy. Our objective was to reach a value of the standard deviation between the experimental and theoretical energy values of the order of 0.02 cm^{-1}. This value is approximately an order of magnitude larger than the experimental error of determination of the line frequencies, 0.001–0.002 cm^{-1}, reported in some studies. However, these estimates often ignore systematic effects and are only valid for strong unblended lines. The experience we gained in using the combination differences to analyze different spectra of the water molecule [16] showed that a value of 0.02 cm^{-1} is a more realistic estimate of the accuracy of energy levels in the infrared and visible wavelength ranges.

Since 1985, the energy value of 26000 cm^{-1} has been the upper boundary of known energy levels of the water molecule in the ground electronic state [17]. Transitions to higher excited vibrational states cannot be observed experimentally by the methods of single-photon spectroscopy, e.g., using Fourier transform spectrometers, because of their low intensity. Only the use of techniques of double and triple laser resonances in conjunction with the variational methods of calculations allowed the energy limit to be shifted beyond the first dissociation threshold that corresponds to the reaction $H_2O \to OH + H$ [18–20]. At present, the problem of determination of the PES for the water molecule in the ground electronic state is quite realistic. However, we do not consider this problem here and restrict ourselves to the optimization of a PES up to 26000 cm^{-1}.

At present, there exist two very accurate semiempirical potentials of the water molecule that are pertinent to our problem. The PES obtained in [14] reproduces the vibration–rotation levels of $H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$ up to 26000 cm^{-1} with a standard deviation of 0.07 cm^{-1}. In [15] the standard deviation was decreased to 0.025 cm^{-1} but at a sacrifice of reducing the energy range down to 18000 cm^{-1}. In describing the energy levels of three isotopologues of the water molecule simultaneously, the upper limit of 18000 cm^{-1} seemed to be more reasonable because experimental data above 18000 cm^{-1} were available only for $H_2{}^{16}O$.

The almost experimental accuracy of variational calculations of the spectra of different isotopologues of the water molecule achieved to date in the range up to 18000 cm^{-1} makes it possible to identify nearly all experimental lines whose frequencies lie below this limit. However, about 200 unidentified lines exist in the range of 18000–26000 cm^{-1} [21]. To solve the problem of the complete analysis of all single-photon spectra of $H_2{}^{16}O$, it remains to obtain a PES that can allow us to perform calculations in the latter range with the experimental accuracy. In our opinion, this problem can be solved using the semiempirical PES obtained in this paper for $H_2{}^{16}O$, which describes the energy levels in the range of 0–26000 cm^{-1} with a standard deviation of 0.022 cm^{-1}. We used different methods to optimize a PES [13, 22] and found that the most accurate PES can be derived by using the combination of these methods described below.

OPTIMIZATION PROCEDURE

Beginning with the paper by Partridge and Schwenke [12], ab initio potentials are used as the starting point in optimizing a PES for the water molecule. In ab initio calculations, the electronic energies are computed for a certain manifold of sets of internal nuclear coordinates (geometries). For example, for a water molecule, the valence coordinates r_1, r_2, and θ can be chosen as these coordinates. Then, using the electronic energy values at these points, the potential energy surface is constructed based on a polynomial in internal nuclear coordinates. The potential thus obtained is called the ab initio PES. Calculations of vibration–rotation energy levels with this potential are frequently called ab initio calculations of the energy levels. It is implied that the method for solving the nuclear Schrödinger equation with this PES is known. At present, there exist several program suites for calculating the nuclear motion of triatomic molecules. In this paper, we used the suite of variational programs DVR3D [23], which allows the nuclear Schrödinger equation to be solved with the required accuracy. The deviation of calculated values of vibration–rotation levels from experimental values is determined by the quality of the potential and corrections to the Born–Oppenheimer (BO) approximation.

Even starting with the same ab initio surface, different optimization strategies lead to different final semiempirical potentials. The simplest and most natural strategy would be to vary all coefficients of the polynomial that appear in the expression for the starting ab initio surface. However, the number of these coefficients usually amounts to several hundred, and the dependence of the energy levels on these coefficients is nonlinear. Under these conditions, the search for the global minimum of the standard deviation, i.e., the average difference between the experimental and calculated energy levels, is a nontrivial problem. There are no predetermined procedures for solving it that could provide a necessary result. A reduction in the number of variable parameters simplifies the problem and can lead to a smaller standard deviation [12].

In [22], it was proposed to use not only the experimental energy levels of a molecule, but also the results of ab initio calculations in the optimization procedure. The inclusion of ab initio energies in the input data involved in the optimization procedure allows one to restrict the discrepancy between the semiempirical PES and the ab initio potential and also to make the procedure more flexible since a larger number of parameters can be varied.

In our previous studies, we used a morphing function to correct an ab initio surface and to improve the agreement between the calculated and experimental energy levels as follows:

$$V_{\text{fit}}(r_1, r_2, \theta) = \hat{f}(r_1, r_2, \theta) V_{\text{ab initio}}(r_1, r_2, \theta).$$

The morphing function is a low-degree polynomial (a fifth-degree polynomial in our case) in powers of valence coordinates r_1, r_2, and θ. A polynomial of a much higher (twelfth) order enters the ab initio potential. Variations in a small (about 30) number of coefficients in the morphing function change both the maximum power and all (about 250) coefficients of the polynomial V_{fit}. Our previous attempts to increase the number of variable parameters in the morphing function did not improve the optimized surface. Thus, we consider the morphing function of the type we have determined to be optimal at present.

In this study, we started with the results of high-precision ab initio electronic structure calculations that allowed us to construct the CVRQD PES [24, 25]. To

Calculated values of band origins of $H_2{}^{16}O$ and differences between calculated and experimental energy values (in cm^{-1})

v_1	v_2	v_3	E_{calc}	$E_{calc} - E_{expt}$	v_1	v_2	v_3	E_{calc}	$E_{calc} - E_{expt}$
0	1	0	1594.767	–0.016	1	4	1	13256.164	
0	2	0	3151.635	–0.004	0	4	2	13453.507	
1	0	0	3657.015	0.038	3	2	0	13640.666	
0	0	1	3755.932	–0.003	2	2	1	13652.641	0.021
0	3	0	4666.789	0.000	1	7	0	13660.048	
1	1	0	5234.965	0.012	4	0	0	13828.264	0.013
0	1	1	5331.268	–0.002	3	0	1	13830.936	0.001
0	4	0	6134.022	–0.007	0	7	1	13835.395	–0.022
1	2	0	6775.081	0.011	0	10	0	13857.058	
0	2	1	6871.509	0.011	1	2	2	13910.883	0.013
2	0	0	7201.537	0.003	0	2	3	14066.179	0.014
1	0	1	7249.823	–0.004	2	0	2	14221.157	0.004
0	0	2	7445.022	0.023	1	0	3	14318.802	0.010
0	5	0	7542.412	0.024	0	0	4	14537.491	0.013
1	3	0	8273.977	–0.001	2	5	0	14578.615	
0	3	1	8373.841	0.011	1	5	1	14647.974	0.002
2	1	0	8761.586	–0.004	0	5	2	14818.464	
1	1	1	8807.004	–0.004	1	8	0	14881.339	
0	6	0	8870.162		0	8	1	14983.827	
0	1	2	9000.119	0.017	3	3	0	15108.085	
1	4	0	9724.196		2	3	1	15119.014	0.014
0	4	1	9833.580	0.004	0	11	0	15295.069	
0	7	0	10086.062	–0.016	4	1	0	15344.498	0.005
2	2	0	10284.367	0.000	3	1	1	15347.955	0.001
1	2	1	10328.729	0.001	1	3	2	15377.718	
0	2	2	10521.730	0.031	0	3	3	15534.701	0.008
3	0	0	10599.690	–0.003	2	1	2	15742.817	–0.021
2	0	1	10613.358	–0.003	1	1	3	15832.748	0.016
1	0	2	10868.870	0.005	2	6	0	15869.627	
0	0	3	11032.389	0.016	1	6	1	15969.030	
1	5	0	11098.359		0	1	4	16046.961	
2	3	0	11767.386	0.004	1	9	0	16071.813	
0	5	1	11242.774	0.001	0	9	1	16160.177	
0	8	0	11253.462		0	6	2	16215.098	
2	3	0	11767.385		3	4	0	16534.269	
1	3	1	11813.215	–0.007	2	4	1	16546.301	0.017
0	3	2	12007.764	0.011	1	4	2	16795.778	
3	1	0	12139.312	0.003	3	2	1	16821.636	–0.000
2	1	1	12151.244	0.010	4	2	0	16823.295	0.024
1	6	0	12380.496		0	12	0	16824.601	
1	1	2	12407.652	0.010	5	0	0	16898.840	0.001
0	9	0	12533.309		0	4	3	16967.491	
0	1	3	12564.997	0.010	2	7	0	17137.584	
0	6	1	12586.261		2	2	2	17227.328	0.051
2	4	0	13204.787		1	7	1	17229.854	

Table. (Contd.)

v_1	v_2	v_3	E_{calc}	$E_{\text{calc}} - E_{\text{expt}}$	v_1	v_2	v_3	E_{calc}	$E_{\text{calc}} - E_{\text{expt}}$
1	2	3	17312.533	0.005	1	4	3	20168.745	
1	10	0	17382.690		0	12	1	20278.898	
0	10	1	17444.533		1	12	0	20310.675	
3	0	2	17458.200	0.014	0	4	4	20386.366	
0	7	2	17490.968		3	2	2	20419.386	
2	0	3	17495.495	0.033	2	2	3	20442.746	0.031
0	2	4	17526.424		3	7	0	20491.477	
1	0	4	17748.097	0.010	2	7	1	20516.130	
3	5	0	17911.189		4	0	2	20533.377	
2	5	1	17927.954		3	0	3	20543.094	0.034
0	0	5	17948.685		1	2	4	20699.925	
1	5	2	18161.496		1	7	2	20720.529	
3	3	1	18265.828	−0.008	1	10	1	20801.217	
4	3	0	18267.151		2	10	0	20832.929	
2	8	0	18331.642		0	2	5	20887.475	
0	5	3	18350.041		2	0	4	20905.978	
5	1	0	18392.786	−0.008	0	10	2	21002.767	
4	1	1	18393.330	−0.015	0	7	3	21005.168	
1	8	1	18423.408		1	0	5	21042.170	
0	13	0	18424.763		4	5	0	21052.001	
0	8	2	18643.527		3	5	1	21053.610	
2	3	2	18674.673		6	1	0	21221.450	0.118
1	3	3	18758.615	0.018	5	1	1	21221.804	0.024
1	11	0	18804.238		0	0	6	21275.132	
0	11	1	18819.165		5	3	0	21313.607	
3	1	2	18955.776		4	3	1	21314.393	0.055
0	3	4	18977.332		2	5	2	21430.268	
2	1	3	18989.941	0.019	1	5	3	21533.567	
3	6	0	19222.662		0	15	0	21628.469	
1	1	4	19242.105		3	8	0	21703.188	
2	6	1	19250.189		2	8	1	21708.647	
0	1	5	19432.909		0	5	4	21764.339	
1	6	2	19440.142		0	13	1	21810.838	
1	9	1	19550.901		3	3	2	21844.710	
2	9	0	19573.604		2	3	3	21867.065	
4	4	0	19677.867		1	13	0	21915.885	
3	4	1	19679.208	−0.015	1	8	2	21971.944	
0	6	3	19720.472		4	1	2	22006.982	
0	9	2	19778.124		3	1	3	22015.478	
5	0	1	19781.102	0.002	1	3	4	22127.796	
6	0	0	19781.310	0.013	1	11	1	22131.841	
5	2	0	19864.792		2	11	0	22165.032	
4	2	1	19865.270	0.014	0	8	3	22221.379	
0	14	0	20029.975		0	3	5	22313.597	
2	4	2	20079.477		0	11	2	22325.606	

Table. (Contd.)

v_1	v_2	v_3	E_{calc}	$E_{\text{calc}} - E_{\text{expt}}$	v_1	v_2	v_3	E_{calc}	$E_{\text{calc}} - E_{\text{expt}}$
4	6	0	22376.759		1	2	5	23934.841	
3	6	1	22378.286		7	1	0	23941.561	
2	1	4	22386.019		6	1	1	23947.069	
1	1	5	22508.134		2	7	2	23953.850	
7	0	0	22529.301	−0.005	3	0	4	23977.312	
6	0	1	22529.437	0.004	4	5	1	23994.122	
6	2	0	22627.268		5	5	0	24013.114	
5	2	1	22629.495		2	10	1	24026.874	
2	6	2	22699.628		2	0	5	24039.908	
0	1	6	22733.449		3	10	0	24079.350	
4	4	1	22738.684		5	3	1	24142.533	
5	4	0	22744.106		6	3	0	24143.058	
2	9	1	22801.038		0	2	6	24162.335	
3	9	0	22872.349		1	7	3	24167.980	
1	6	3	22915.335		1	0	6	24292.429	
1	9	2	23056.950		1	10	2	24300.657	
0	6	4	23146.854		0	7	4	24424.882	
3	4	2	23232.325		0	10	3	24453.804	
1	14	0	23252.580		0	0	7	24511.497	
2	4	3	23253.747		3	5	2	24577.112	
0	9	3	23308.864		2	5	3	24604.843	
0	14	1	23356.632		5	1	2	24795.787	
5	0	2	23400.966		4	1	3	24807.287	
4	0	3	23405.254		2	13	0	24817.101	
4	2	2	23466.678		3	8	1	24848.493	
3	2	3	23474.708		1	5	4	24864.851	
1	4	4	23520.352		4	8	0	24874.664	
2	12	0	23549.418		3	3	3	24908.313	
1	12	1	23595.810		4	3	2	24914.135	
0	16	0	23644.022		1	13	1	24918.326	
4	7	0	23655.941		0	5	5	25073.588	
3	7	1	23658.328		1	15	0	25085.975	
0	4	5	23710.326		8	0	0	25120.250	
0	12	2	23776.250		7	0	1	25120.263	0.015
2	2	4	23823.364		0	13	2	25145.615	

calculate the electronic energies, we used the multireference configuration interaction (MRCI) method, and the calculated results were obtained for 1495 geometries. The electronic energy value for each set of internal nuclear coordinates was extrapolated to the complete basis set (CBS) limit. Then we added several corrections, including the correction for correlation of the core and valence (CV) electrons and the adiabatic (DBOC), relativistic (REL), and quantum-electrodynamics (QED) corrections as follows [23, 24]:

$$V_{\text{CVRQD}} = V_{\text{CBS}} + V_{\text{CV}} + V_{\text{DBOC}} + V_{\text{REL}} + V_{\text{QED}}.$$

The set of experimental data on the energy levels of $H_2{}^{16}O$ used by us in the optimization procedure consisted of 1508 levels with $J = 0$, 2, and 5 taken from the database of [16]. Using the CVRQD PES the standard deviation is about 1 cm^{-1} for the chosen dataset.

In order to avoid nonphysical distortions of the PES, we imposed additional restrictions on the deviation of the optimized surface from the starting ab initio PES upon variations in potential parameters as proposed in [22]. This was accomplished by simultaneously optimizing the variable parameters with respect to both the experimental values of energy levels $E_i^{\exp}$ and the ab initio values of the potential energy surface V_k^{ai}. For this purpose, we used 1495 CBS ab initio energy values (without allowance for corrections to the BO approximation) that covered the PES up to 56600 cm^{-1}. Thus, in optimizing 240 potential parameters, in addition to 1508 experimental energy levels, 1495 constraints were imposed, the sample of which covers all the necessary deformations of the molecular geometry. The imposed constraints eliminate the difficulties caused by shortage of experimental data that are typical of this problem and lead to the need to reduce the set of variable parameters. In this case, the high quality of the starting ab initio PES used as an additional constraint is of importance. Indeed, if the ab initio PES is very close to the "real" potential surface of water, the imposed constraints allow the region of values of the variable parameters to be narrowed significantly.

All calculations of the nuclear motion were carried out using the DVR3D program suite with the Radau coordinates. In all calculations, we used 29 radial and 40 angular grid points. In solving the vibrational problem, the final matrices of dimension 1500 were diagonalized. For the rotational problems, the final matrices had dimensions of $400(J + 1 - p)$, where J is the total angular momentum quantum number and p is the parity. The number of grid points and the dimensions of matrices chosen sufficed to ensure the convergence of all the energies of interest to us. Nuclear masses were used in all calculations.

RESULTS OF OPTIMIZATION

The optimization performed by the method of [22] using the experimental energy levels and the ab initio energies allowed us to obtain a standard deviation of 0.024 cm^{-1} (for the energy levels), i.e., almost two orders of magnitude as low as a value of 1 cm^{-1} characteristic of the starting ab initio PES. Another important way to estimate the constructed surface is to compare it with the starting ab initio PES, which yields a standard deviation of only 9 cm^{-1} for 1495 ab initio energy values below 56600 cm^{-1}.

We decided to use only the CBS energies without the adiabatic, relativistic, and other corrections as an additional constraint because, first, the expansion parameters of the CBS PES are involved in the optimization and, second, only the CBS data are sufficiently complete and accurate, which is required for the simultaneous optimization procedure. Clearly, the corrections to the CBS energies represented in different functional forms also have a significant effect on the optimization of the PES, which is difficult to take into account in the adopted procedure of simultaneous optimization. In order to solve this problem and to further improve the properties of the optimized PES, we morphed it by multiplying the PES by the morphing function and varying the corresponding 24 parameters. The use of the resulting surface allowed us to decrease the standard deviation to 0.022 cm^{-1}. In varying the parameters of the morphing function, we do not keep watch on the deviation of V_{fit} from the starting ab initio potential, and instead focus our attention only on the standard deviation of the energy levels.

As before [14, 15], we used additional operators J_{xx}, J_{yy}, and J_{zz} from [26] to take into account the influence of nonadiabatic effects on highly excited rotational states. The coefficients in front of these operators were additional adjustable parameters and were optimized in calculations of the energy levels with $J = 20$. Their values are 0.06, 0.06, and –0.21, respectively.

To demonstrate the accuracy of the calculated spectrum of $H_2{}^{16}O$ achieved using the optimized PES, in the table, we present the calculated values of the band origins and the differences between the calculated and the experimental energy values for the vibrational states for which the band origins were measured experimentally. Approximate vibrational quantum numbers were assigned in accordance with the results of [27].

CONCLUSIONS

In this paper, a semiempirical PES was obtained that allows the vibration–rotation levels of the $H_2{}^{16}O$ molecule in the range up to 26000 cm^{-1} with the values of the total angular momentum quantum number $J = 0$, 2, and 5 to be calculated with a standard deviation of 0.022 cm^{-1}. The error of variational calculations with the use of the new PES nearly coincides with the average experimental error of determination of most energy levels for the major isotopologue of the water molecule in the infrared and visible ranges. The obtained root-mean-square deviation is smaller than the average linewidths (about 0.03 cm^{-1}). This averages that the calculated line centers fall within the experimental linewidths, and the spectrum can be identified by relating an experimental line to the nearest theoretical line.

Several years ago, a task group of spectroscopists with wide experience in the study of the spectrum of the water molecule was established under the aegis of the International Union of Pure and Applied Chemistry (IUPAC) [28]. The group is working on the project titled "Database of Water Transitions from Experiment and Theory." The objective of this project is compilation and verification of the vast amount of experimental and theoretical data on the spectrum of the water molecule gathered over decades of investigations. The important goals of the project include theoretical calculations with experimental accuracy that would allow one to verify analyses of the spectra performed in original studies. At present, the work on the spectra of the isotopologues $H_2{}^{17}O$ and $H_2{}^{18}O$ [29], $HD^{16}O$, $HD^{17}O$, and $HD^{18}O$ [30] has been completed. The amount of information accumulated on the major isotopologue $H_2{}^{16}O$ of the water molecule is an order of magnitude larger than the data on other isotopologues, and the study on this isotopologue is currently underway. Calculations using the potential derived in this paper will be of great benefit in this study.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 09-02-00053.

REFERENCES

1. B. M. Dinelli, O. L. Polyansky, and J. Tennyson, J. Chem. Phys. **103**, 10 433 (1995).
2. X. C. Huang, D. W. Schwenke, and T. J. Lee, J. Chem. Phys. **129**, 214 304 (2008).
3. V. G. Tyuterev, L. Regalia-Jarlot, D. W. Schwenke, S. A. Tashkun, and Y. G. Borkov, Comp. Ren. Phys. **5**, 189 (2004).
4. S. N. Yurchenko, J. Zheng, H. Lin, P. Jensen, and W. Thiel, J. Chem. Phys. **123**, 134 308 (2005).
5. A. J. C. Varandas and S. P. J. Rodrigues, J. Phys. Chem. A **110**, 485 (2006).
6. R. J. Barber, J. Tennyson, G. J. Harris, and R. N. Tolchenov, Mon. Not. R. Astron. Soc. **368**, 1087 (2006).
7. G. Tinetti, A. Vidal-Madjar, M. C. Liang, J. P. Beaulieu, Y. Yung, S. Carey, R. J. Barber, J. Tennyson, I. Ribas, N. Allard, G. E. Ballester, D. K. Sing, and F. Selsis, Nature **448**, 169 (2007).
8. S. Carter and N. C. Handy, J. Chem. Phys. **87**, 4294 (1987).
9. P. Jensen, S. A. Tashkun, and V. G. Tyuterev, J. Mol. Spectrosc. **168**, 271 (1994).
10. O. L. Polyansky, P. Jensen, and J. Tennyson, J. Chem. Phys. **101**, 7651 (1994).
11. O. L. Polyansky, P. Jensen, and J. Tennyson, J. Chem. Phys. **105**, 6490 (1996).
12. H. Partridge and D. W. Schwenke, J. Chem. Phys. **106**, 4618 (1997).
13. S. V. Shirin, O. L. Polyansky, N. F. Zobov, P. Barletta, and J. Tennyson, J. Chem. Phys. **118**, 2124 (2003).
14. S. V. Shirin, O. L. Polyansky, N. F. Zobov, R. I. Ovsyannikov, A. G. Csaszar, and J. Tennyson, J. Mol. Spectrosc. **236**, 216 (2006).
15. S. V. Shirin, N. F. Zobov, R. I. Ovsyannikov, O. L. Polyansky, and J. Tennyson, J. Chem. Phys. **128**, 224 306 (2008).
16. J. Tennyson, N. F. Zobov, R. Williamson, O. L. Polyansky, and P. F. Bernath, J. Phys. Chem. Ref. Data. **30**, 735 (2001).
17. J. M. Flaud, C. Camy-Peyret, J. Y. Mandin, J. P. Chevillard, J. W. Brault, D. A. Ramsay, M. Vervloet, and J. Chauville, J. Mol. Spectrosc. **113**, 208 (1985).
18. P. Maksyutenko, J. S. Muenter, N. F. Zobov, S. V. Shirin, O. L. Polyansky, T. R. Rizzo, and O. V. Boyarkin, J. Chem. Phys. **126**, 241 101 (2007).
19. M. Grechko, P. Maksyutenko, T. R. Rizzo, O. V. Boyarkin, N. F. Zobov, S. V. Shirin, and O. L. Polyansky, J. Phys. Chem. A **112**, 10539 (2008).
20. M. Grechko, O. V. Boyarkin, T. R. Rizzo, P. Maksyutenko, N. F. Zobov, S. V. Shirin, L. Lodi, J. Tennyson, A. G. Csaszar, and O. L. Polyansky, J. Chem. Phys. **131**, 221 105 (2009).
21. R. N. Tolchenov, N. F. Zobov, O. L. Polyansky, J. Tennyson, O. Naumenko, M. Carleer, P. F. Coheur, S. Folly, A. Jenouvrier, and A. C. Vandaele, J. Mol. Spectrosc. **233**, 68 (2005).
22. S. N. Yurchenko, M. Carvajal, P. Jensen, F. Herregodts, and T. R. Huet, J. Chem. Phys. **290**, 59 (2003).
23. J. Tennyson, M. A. Kostin, P. Barletta, G. J. Harris, O. L. Polyansky, J. Ramanlal, and N. F. Zobov, Comput. Phys. Commun. **163**, 85 (2004).
24. O. L. Polyansky, A. G. Csaszar, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke, and P. J. Knowles, Science **299**, 539 (2003).
25. P. Barletta, S. V. Shirin, N. F. Zobov, O. L. Polyansky, J. Tennyson, E. F. Valeev, and A. G. Csaszar, J. Chem. Phys. **125**, 204 307 (2006).
26. D. W. Schwenke, J. Phys. Chem. A **105**, 2352 (2001).
27. A. G. Csaszar, E. Matyus, T. Szidarovszky, L. Lodi, N. F. Zobov, S. V. Shirin, O. L. Polyansky, and J. Tennyson, J. Quant. Spectrosc. Radiat. **111**, 1043 (2010).
28. http://www.iupac.org/web/ins/2004-035-1-100.
29. J. Tennyson, P. F. Bernath, L. R. Brown, A. Campargue, M. R. Carleer, A. G. Csaszar, R. R. Gamache, J. T. Hodges, A. Jenouvrier, O. V. Naumenko, O. L. Polyansky, L. S. Rothman, R. A. Toth, A. C. Vandaele, N. F. Zobov, L. Daumont, A. Z. Fazliev, T. Furtenbacher, I. E. Gordon, S. N. Mikhailenko, and S. V. Shirin, J. Quant. Spectrosc. Radiat. **110**, 573 (2009).
30. J. Tennyson, P. F. Bernath, L. R. Brown, A. Campargue, M. R. Carleer, A. G. Csaszar, L. Daumont, R. R. Gamache, J. T. Hodges, O. V. Naumenko, O. L. Polyansky, L. S. Rothman, A. C. Vandaele, N. F. Zobov, A. Z. Fazliev, T. Furtenbacher, I. E. Gordon, S. N. Mikhailenko, and B. A. Voronin, J. Quant. Spectrosc. Radiat. Transfer **111**, 2160 (2010).