Effective Pade Hamiltonian Operator and Its Application for Treatment of $H_2{}^{16}O$ Rotational Spectrum in the Ground State

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Both microwave and infrared data on frequencies of rotational transitions in the $H_2{}^{16}O$ ground state are fitted for the first time within the limits of experimental errors. This fitting is based on a representation of the effective rotational Hamiltonian operator in the form of a Pade operator. New experimental data on frequencies of microwave transitions in the submillimeter wave region are obtained.

INTRODUCTION

One of the most interesting problems of high resolution molecular spectroscopy at present is the problem of treatment of vibration–rotational spectra of molecules with strong nonrigidity effects. We include in this class of molecules the following types: (1) molecules with small moments of inertia; (2) molecules in vibrational states perturbed by strong accidental resonances; (3) molecules with several equilibrium configurations separated by a small potential barrier. We emphasize that the class of molecules considered includes such classical subjects of molecular spectroscopy as H_2O, NH_3, CH_3, and many other small molecules whose vibrational–rotational spectra are significant from the point of view of their applications. The problem lies in the fact that traditional methods of the theory of molecular spectra when fitting modern experimental data for molecules with strong nonrigidity effects have considerable difficulties caused by a bad convergence or even divergence of the perturbation theory series used. Let us consider briefly the reason for this. The most fully developed method treating vibration–rotational spectra of molecules consists of construction of effective Hamiltonian operators by the operative perturbation theory (see, for example, Ref. (*1*)). In particular, for each nondegenerate isolated vibrational state an effective rotational operator is constructed in the form of a finite Taylor series in components of the angular momentum **J**. All the phenomenological constants included in this operator (which we henceforth call spectroscopic constants) can be, in principle, expressed in terms of structural and force constants of the molecule referring to its equilibrium configuration (*1, 2*). Naturally, the interpretation is valid if the finite Taylor series converges rather quickly at $J \sim 1$. It is assumed that this requirement is fulfilled at least for isolated vibrational states. However, when fitting experimental data one needs series convergence for angular momentum values which correspond to actually observed transitions. This requirement is significantly stronger, since each term of the series infinitely increases with total angular momentum and the increase of the term is faster, the higher the order of its smallness parameter.

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Therefore, the value of the total angular momentum has an upper limit for which the traditional series of the perturbation theory converges. As an example, Table I displays bounds of convergence for some molecules arranged by their nonrigidity increase. It can be easily seen that for rigid molecules (a typical representative is the OCS molecule in the ground vibrational state) this bound is rather large and as a result all experimental data available at present lie considerably below it. On the contrary, for nonrigid molecules there are experimental data lying either close to this bound (PH_3 and H_2S in the ground state) or even crossing it (H_2O in the ground state and PH_3 in the vibrational state $v_2 = 1$). It should be underlined that slow convergence of the perturbation theory series which takes place for molecules PH_3 and H_2S in the ground state also makes fitting of the spectrum within the limits of experimental errors impossible because of the necessity of allowing for a rather large number of terms in this series.

An effective way out of this situation is the use of the rotational Hamiltonian operator in the form of an infinite Taylor series by the method of partial summation of this series. We write this partial sum in the form of a Pade operator:

$$H_{\text{Pade}} = \frac{1}{2} \left(H \frac{1}{1+h} + \frac{1}{1+h} H \right). \tag{1}$$

Operators H and h represent a finite Taylor series in angular momentum components and in the general case these operators do not commute. The main advantage of the approach based on a Pade Hamiltonian operator is associated with the qualitatively correct asymptotic behavior of the Pade operator both for small and large values of angular moment. Thus, it is natural that fitting of experimental data by means of Pade Hamiltonian operator for molecules with strong nonrigidity effects will be significantly more efficient than fitting with the help of a standard Hamiltonian operator. An indication of this is the circumstance that during the last decade Pade approximants were successfully used for reformulation of the Rayleigh–Schrödinger perturbation theory (RSPT). It is shown by numerous specific examples (for instance, for some anharmonic oscillators (3)) that in the case of a slowly converging RSPT series the series of its Pade approximants converges rapidly to an exact solution and in the case of a diverging RSPT series the series of its Pade approximants converges all the same (though sometimes slowly) to an exact solution. Besides, the following general rigorous result is known (4): if the diverging perturbation theory series is of the Stiltjes type, the series of its Pade approximants converges to an exact solution and converging

TABLE I

Limits of Quantum Number Convergence of Total Angular Momentum of Perturbation Theory Series in a Traditional Description of Rotational Spectra for Some Molecules Arranged in Order of Increasing Nonrigidity

OCS	PH_3	H_2S	H_2O	PH_3
V=0	V=0	V=0	V=0	$v_2=1$
700	40	20	5	2

series of Pade approximants yielding upper and lower bounds of the exact solution can be pointed out.

In the present paper, we consider the application of the effective Pade Hamiltonian operator for fitting of the rotation spectrum of $H_2{}^{16}O$ molecule in the ground state. This molecule is the most important representative of the class of molecules H_2X, i.e., the class most difficult to fit by traditional methods.

I. EFFECTIVE ROTATIONAL PADE HAMILTONIAN OPERATOR FOR A NONDEGENERATE VIBRATIONAL STATE

The effective rotational Pade Hamiltonian operator was successfully used by us for fitting frequencies of rotational transitions of PH_3 in the ground state (5), frequencies of rotational transitions of H_2S in the ground state (6), and frequencies of rotational transitions of PH_3 in the ground and excited $v_2 = 1$ vibrational states together with vibration–rotational transitions of the fundamental band v_2 (7) (see also review (8)). We stress that the use of a Pade operator permitted us (7) to conserve completely the concept of the effective rotational Hamiltonian operator for the case of perturbed vibrational states and made it possible to fit the vibrational state $v_2 = 1$ by analogy with an isolated vibrational state. In all these papers we used an effective Pade Hamiltonian operator with operators H and h in the form

$$H = \sum_{k=1}^{n} H_k \qquad h = \sum_{k=1}^{n} h_k \qquad (2)$$

where the term with index k includes the product of angular momentum components of the summary power $2k$ in the reduced Watson formulation. This leads to the following asymptotic behavior of H_{Pade}:

$$\lim_{J \to 0} H_{\text{Pade}} = 0 \qquad \lim_{J \to \infty} H_{\text{Pade}} = \text{const.} \qquad (3)$$

However, we pointed out in Refs. (7, 8) that there are reasons to assume that the choice of operators H and h in the form

$$H = -E + \sum_{k=1}^{n-1} H_k \qquad h = \sum_{k=1}^{n} h_k \qquad (4)$$

will result in a reduction of the number of phenomenological constants necessary for the spectrum fitting. The main reason consists of the more natural asymptotic behavior of H_{Pade}:

$$\lim_{J \to 0} H_{\text{Pade}} = -E \qquad \lim_{J \to \infty} H_{\text{Pade}} = 0 \qquad (5)$$

and a possibility arises to include in the treatment very important information on the depth of the molecular potential well.

Since for the molecule $H_2{}^{16}O$ the problem of the number of phenomenological constants necessary for fitting the experimental data available on frequencies of rotational transitions in the ground state is quite serious (a very nonrigid molecule and a very large number of very precise experimental data), the choice of a more effective form of Pade operator was very important. Therefore, we performed a practical

comparison of both forms. As had been assumed, the second form has considerable advantages compared with the first one. As a consequence, we shall henceforth use the effective Pade operator with operators H and h in form (4) with $n = 5$:

$$h_2 = X'J_x^2 + Y'J_y^2 + Z'J_z^2$$

$$h_4 = -\Delta'_J J^4 - \Delta'_{Jk} J^2 J_z^2 - \Delta_k J_z^4 - 2\delta'_J (J_x^2 - J_y^2) - \delta'_k F_2$$

$$h_6 = H'_J J^6 + H'_{Jk} J^4 J_z^2 + H'_{kJ} J^2 J_z^4 + H'_k J_z^6 + 2h'_J J^4 (J_x^2 - J_y^2) + h'_{Jk} J^2 F_2 + h'_k F_4$$

$$h_8 = L'_J J^8 + L'_{JJk} J^6 J_z^2 + L'_{Jk} J^4 J_z^4 + L'_{Jkk} J^2 J_z^6 + L'_k J_z^8$$

$$+ 2l'_J J^6 (J_x^2 - J_y^2) + l'_{Jk} J^4 F_2 + l'_{kJ} J^2 F_4 + l'_k F_6$$

$$h_{10} = M'_J J^{10} + M'_{JJk} J^8 J_z^2 + M'_{Jk} J^6 J_z^4 + M'_{kJ} J^4 J_z^6 + M'_{Jkk} J^2 J_z^8 + M'_k J_z^{10}$$

$$+ 2m'_J J^8 (J_x^2 - J_y^2) + m'_{JJk} J^6 F_2 + m'_{Jk} J^4 F_4 + m'_{Jkk} J^2 F_6 + m'_k F_8. \quad (6)$$

Here $F_k = J_z^k(J_x^2 - J_y^2) + (J_x^2 - J_y^2)J_z^k$. Operators H_k ($k = 2, 4, 6, 8$) have an analogous form, except that the notation of constants in them lacks a prime. It can be easily seen that this model in the maximum variant contains 60 parameters.

Consider the problem of interpretation of the Pade Hamiltonian operator constants. Upon expanding the Pade operator (1) in an infinite Taylor series, all coefficients of this series will be expressed in terms of the Pade operator constants. This infinite series sum up for any angular momentum and for its formal construction the infinitesimal parameter is not necessary. Therefore, the interpretation of quadratic, quartic, and sextic coefficients of the Taylor series available now may be used in work with the Pade operator even in the case of a complete impossibility of fitting the spectrum by representation of the Hamiltonian operator in the form of a finite Taylor series. The specific transition from phenomenological constants of the Pade Hamiltonian operator to spectroscopic constants of the Hamiltonian operator in the Watson reduced formulation can be conveniently divided into two stages. In the first stage H_{Pade} is expanded in a Taylor series

$$H_{\text{Pade}} \simeq H - \frac{1}{2}(Hh + hH) + \cdots = -E + q_\alpha J_\alpha^2 + \frac{1}{4}\tau_{\alpha\alpha\beta\beta}J_\alpha^2 J_\beta^2 + \cdots. \quad (7)$$

Here we give only the dependence of quadratic coefficients of this series on Pade operator constants to point out the orientation of Cartesian axes chosen by us with respect to principal axes of the molecule:

$$A = q_z = Z + EZ'$$

$$B = q_x = X + EX'$$

$$C = q_y = Y + EY'. \quad (8)$$

In the second stage, it is necessary to perform a series of unitary transformations of the Hamiltonian operator (7). In particular, the transformation generator reducing quadratic terms to Watson formulation has the form

$$S = \frac{1}{4}(X' - Y')(J_x J_y J_z + J_z J_y J_x). \quad (9)$$

In this case we obtain the following expressions for quadratic and quartic Watson constants with an accuracy to sextic contributions using phenomenological constants of Pade operator:

$$q_x^{sp} = q_x + (X' - Y')(q_z - q_y)$$

$$q_y^{sp} = q_y + (X' - Y')(q_x - q_z)$$

$$q_z^{sp} = q_z + (X' - Y')(q_y - q_x)$$

$$\Delta_J^{sp} = \Delta_J + E\Delta_J' + \frac{1}{2}(q_x X' + q_y Y')$$

$$\Delta_{JK}^{sp} = \Delta_{JK} + E\Delta_{JK}' - \frac{3}{2}(q_x X' + q_y Y') + \frac{1}{2}(q_x Z' + q_z X' + q_y Z' + q_z Y' + q_x Y' + q_y X')$$

$$\delta_J^{sp} = \delta_J + E\delta_J' + \frac{1}{4}(q_x X' - q_y Y')$$

$$\delta_k^{sp} = \delta_k + E\delta_k' - \frac{1}{2}(q_x X' - q_y Y') + \frac{3}{4}q_z(X' - Y')$$

$$+ \frac{1}{4}q_x(Y' + Z') - \frac{1}{4}q_y(X' + Z'). \quad (10)$$

It is convenient to refine these couplings and obtain similar ones for spectroscopic constants of higher orders by means of a system of analytical calculations with a computer (see, for example Ref. (9)).

It is clear that in making the transition to spectroscopic constants we use only a small part of the information on the force field of the molecule contained in the Pade operator constants. Unfortunately, the lack of a consistent theory of construction of the effective Hamiltonian operator in the Pade form prevents us from giving another variant for the use of this information.

2. EXPERIMENT

At present we investigate the H_2O rotational spectrum experimentally in the frequency region 300–900 GHz by a submillimeter spectrometer RAD (10). Note that though the water molecule is one of the most important subjects of high resolution spectroscopy, the number of rotational spectrum frequencies measured by microwave methods is not large. Thus, frequencies of only 15 transitions were measured for $H_2^{16}O$ ground state (11). This situation is explained by the following reasons. First, the microwave region contains only a small number of strong transitions of the water molecule. Second, for relatively weak transitions of this region centrifugal effects are, as a rule, so strong that traditional methods of the theory of molecular spectra encounter considerable difficulties making an attempt to predict their frequencies with an accuracy sufficient for indentification. Microwave rotational transitions for $H_2^{16}O$ ground state measured by us before writing this paper and those known earlier are presented in Table II.

The position of the line center of the rotational spectrum in a water molecule

TABLE II

Experimental and Calculated Frequencies of Microwave Rotational Transitions
for $H_2^{16}O$ in the Ground State

Transition Upper state — Lower state $\nu_{obs}(\Delta\nu_{obs})$	Obs.Freq.(MHz)	Cal.Freq.(MHz) $\nu_{cal}(\Delta\nu_{cal})$	$\nu_{cal} - \nu_{obs}$ [a] The present paper. KHz	$\nu_{cal} - \nu_{obs}$ [b] KHz	$\nu_{cal} - \nu_{obs}$ [c] KHz
$6_{16} - 5_{23}$	22 235.07985(5)	22 235.07985(5)	0		− 14 136
$3_{13} - 2_{20}$	183 310.0906(15)	183 310.0906(15)	0		9 851
$10_{29} - 9_{36}$	321 225.64(24)	321 225.64(24)	0		2 410
$5_{15} - 4_{22}$	325 152.919(27)	325 152.914(27)	5		− 14 153
$4_{14} - 3_{21}$	380 197.372(25)	380 197.376(25)	− 4		− 4 485
$7_{53} - 6_{60}$	437 346.67(20)	437 346.30(16)	370		− 71 760
$6_{43} - 5_{50}$	439 150.812(53)	439 150.875(52)	− 63		− 29 918
$7_{52} - 6_{61}$	443 018.30(21)	443 018.32(17)	− 20		− 72 330
$4_{23} - 3_{30}$	448 001.075(22)	448 001.079(22)	− 4		25 133
$6_{42} - 5_{51}$	470 888.95(19)	470 888.67(18)	280		− 29 790
$5_{33} - 4_{40}$	474 689.127(72)	474 689.034(70)	93		17 260
$6_{24} - 7_{17}$	488 491.13(38)	488 491.32(36)	− 190		5 490
$8_{63} - 7_{70}$	503 568.382(100)*	503 568.280(78)	102	− 158 100	
$8_{62} - 7_{71}$	504 482.635(100)*	504 482.751(78)	− 116	− 158 000	
$1_{10} - 1_{01}$	556 936.002(89)	556 936.004(88)	− 2		− 442
$5_{32} - 4_{41}$	620 700.95(20)*	620 701.07(20)	− 120		21 080
$9_{73} - 8_{80}$	645 766.010(100)*	645 765.980(87)	30		
$9_{72} - 8_{81}$	645 905.620(100)*	645 905.581(87)	39		
$2_{11} - 2_{02}$	752 033.23(49)	752 033.10(31)	130		3 620

[a] The present paper.
[b] Ref. (*16, 11*) (see text).
[c] Ref. (*17*).
Notes: The asterisk denotes the transitions whose frequencies were measured in the present paper. All indicated errors correspond to the root mean square deviation.

strongly depends on pressure. Therefore, line frequencies were measured at various pressures in an absorbing cell and extrapolation to zero pressure was performed. All measurements were made at room temperature.

3. ANALYSIS

When fitting the frequencies of rotational transitions of $H_2^{16}O$ in the ground state we used all known microwave data (19 transitions displayed in Table II) and rather precise ir data obtained recently using Fourier spectroscopy methods (20 transitions of paper (*12*) in the region 28–50 cm⁻¹ represented in Table III and more than 400 transitions of paper (*13*) in the region 50–750 cm⁻¹ which are not repeated here because of space limitations. The maximum value of the quantum number of the angular momentum for the experimental data used is 17, several times greater than

TABLE III

Experimental and Calculated Frequencies of IR Rotational Transitions in the Frequency Region below
50 cm^{-1} for H$_2$^{16}O in the Ground State

Transition Upper state	Transition Lower state	Observed frequency (cm^{-1})	Calculated frequency (cm^{-1})	Obs.-calc. frequency in cm^{-1}·10^3
10(5,6)	-11(2,9)	28.054	28.0552(14)	-1.22
9(2,8)	- 8(3,5)	30.2294	30.22780(27)	1.60
4(2,2)	- 3(3,1)	30.5605	30.560340(27)	0.16
5(2,4)	- 4(3,1)	32.3664	32.366054(54)	0.35
2(0,2)	- 1(1,1)	32.9539	32.953736(21)	0.16
3(1,2)	- 3(0,3)	36.6036	36.604162(25)	-0.56
1(1,1)	- 0(0,0)	37.1373	37.1371104(90)	0.19
7(2,5)	- 8(1,8)	38.248	38.247212(66)	0.79
3(1,2)	- 2(2,1)	38.4648	38.464319(33)	0.48
6(3,4)	- 5(4,1)	38.6383	38.63706(18)	1.24
3(2,1)	- 3(1,2)	38.7909	38.790430(66)	0.47
7(4,4)	- 6(5,1)	39.1125	39.11091(41)	1.59
4(2,2)	- 4(1,3)	40.2829	40.282313(74)	0.59
2(2,0)	- 2(1,1)	40.9881	40.987899(44)	0.20
7(4,3)	- 6(5,2)	42.6383	42.63799(41)	0.31
8(2,7)	- 7(3,4)	43.2452	42.24350(27)	1.70
8(4,5)	- 9(1,8)	43.6296	43.62920(55)	0.40
6(2,5)	- 5(3,2)	44.1001	44.09906(12)	1.04
7(4,4)	- 8(1,7)	44.858	44.85395(45)	4.05
5(2,3)	- 5(1,4)	47.055	47.052933(75)	2.07

the convergence bound for the traditional method of treatment pointed out in Table I. Note that convergence bounds in Table I for nonrigid molecules are obtained from the conditions $\|h\| \sim 1$.

The value for the potential well depth of the water molecule was taken to be

$$E = 2.5 \times 10^9 \text{ MHZ} \simeq 10.3 \text{ eV}.$$

This value equals twice the energy of the chemical bond dissociation of OH in the water molecule (14). It is important to emphasize that the Pade Hamiltonian operator admits numerous versions of treatment corresponding to local minima of the proximity functional between experimental data and their theoretical analogs. The range in possibilities of fitting for different versions can be very large. Due to this the technical side of a treatment based on the Pade Hamiltonian operator is still more difficult than that for the traditional approach. This situation will change as we gain more and more experience working with the Pade Hamiltonian operator. The algorithm of the solution of the inverse spectroscopic problem applied in this paper is the improved modification of the algorithm described in Refs. (9, 15). This modification will be published separately.

The principal result of the treatment is the fact that we succeeded in fitting the given experimental data within the limits of their errors for the first time. The phenomenological constants of the Pade operator obtained here are displayed in Table IV.[1] The frequencies of all microwave transitions and ir transitions in the region 28–

[1] We do not give the correlation coefficient matrix of these constants because of its considerable bulkiness.

TABLE IV

Phenomenological Parameters of the Effective Pade Hamiltonian Operator
for $H_2^{16}O$ in the Ground State

Numerator constants			Denominator constants	
Y	915 286.012 337(59245046)	MHz	Y'	$-0.254\ 664\ 905\ 927(23694981)10^{-3}$
Z	-9198 791.761 9081(9583577466)	MHz	Z'	$0.401\ 392\ 894\ 57911(3833443235)10^{-2}$
X	-1982 858.642 90(12239005)	MHz	X'	$0.967\ 012\ 875\ 120(48945050)10^{-3}$
Δ_J	- 385.273 022 (2082605)	MHz	Δ'_J	$0.992\ 450\ 478(8333229)10^{-7}$
Δ_{JK}	- 10 232.196 851(57926910)	MHz	Δ'_{JK}	$0.351\ 016\ 5884(23166353)10^{-5}$
Δ_K	- 6204.627 882(99493780)	MHz	Δ'_K	$0.211\ 246\ 9374(39801062)10^{-5}$
δ_J	- 634.904 876(527478)	MHz	δ'_J	$0.210\ 810\ 218(210661)10^{-6}$
δ_K	- 3383.651 96(1152948)	MHz	δ'_K	$0.113\ 756\ 7978(4608154)10^{-5}$
H_J	227.3338(370981)	KHz	H'_J	$-0.124\ 5396(148421)10^{-9}$
H_{JK}	- 22 261.2208(38055741)	KHz	H'_{JK}	$0.856\ 744\ 35(15222600)10^{-8}$
H_{KJ}	- 66 914.524(3360866)	KHz	H'_{KJ}	$0.250\ 772\ 70(1344041)10^{-7}$
H_K	- 31 678.362(1995642)	KHz	H'_K	$0.127\ 964\ 634(7988427)10^{-7}$
h_J	- 88.1938(136945)	KHz	h'_J	$0.122\ 64(547661)10^{-12}$
h_{JK}	- 2147.622(269488)	KHz	h'_{JK}	$0.526\ 365(107693)10^{-9}$
h_K	12 648.597(3767885)	KHz	h'_K	$-0.507\ 6675(1504708)10^{-8}$
L_J	- 0.261 6295(7710745)	KHz	L'_J	$0.968\ 238(3079633)10^{-13}$
L_{JJK}	2.0943(194921)	KHz	L'_{JJK}	$0.169\ 63(778967)10^{-12}$
L_{JK}	631.129 74(7883996)	KHz	L'_{JK}	$-0.246\ 464\ 92(3160989)10^{-9}$
L_{JKK}	69.2982(376801)	KHz	L'_{JKK}	$-0.212\ 684(151039)10^{-10}$
L_K	48.6889(278542)	KHz	L'_K	$-0.185\ 901(111495)10^{-10}$
l_J	0.187 2785(3613067)	KHz	l'_J	$-0.711\ 513(1442656)10^{-13}$
l_{JK}	4.353 971(6471757)	KHz	l'_{JK}	$-0.141\ 3257(2580235)10^{-11}$
l_{KJ}	- 81.900 80(5460167)	KHz	l'_{KJ}	$0.319\ 2059(2184911)10^{-10}$
l_K	- 12.3457(1098255)	KHz	l'_K	$0.422\ 647(4416280)10^{-11}$
			M_J	$-0.7(4756)10^{-19}$
			M_{JJK}	$-0.217(1174)10^{-15}$
			M_{JK}	$-0.3757(420)10^{-13}$
			M_{KJ}	$-0.4472(779)10^{-13}$
			M_{JKK}	$-0.1043(821)10^{-13}$
			M_K	$0.120(497)10^{-14}$
			m_J	$-0.1358(2212)10^{-16}$
			m_{JJK}	$-0.6062(4210)10^{-15}$
			m_{JK}	$0.964(3342)10^{-15}$
			m_{JKK}	$0.60(966)10^{-15}$
			m_K	$0.496(542)10^{-14}$

50 cm^{-1} used in the treatment and calculated by these constants are represented in Tables II and III, respectively. For ir transitions of paper (13) in the region 50–750 cm^{-1} we give only rms deviations obtained when fitting:

$$0.1 \leqslant I \leqslant 1 \qquad \delta \simeq 1.5 \times 10^{-3} \text{ cm}^{-1}$$
$$0.01 \leqslant I < 0.1 \qquad \delta \approx 1.5 \times 10^{-3} \text{ cm}^{-1}$$
$$0.001 \leqslant I < 0.01 \qquad \delta \approx 2.0 \times 10^{-3} \text{ cm}^{-1}$$
$$I < 0.001 \qquad \delta \approx 3.3 \times 10^{-3} \text{ cm}^{-1}$$

Here I is the relative intensity of transitions given in Ref. (13) and δ is the rms deviation obtained by us for transitions of the indicated intensity. These values agree well with apparatus characteristics mentioned in Ref. (13).

Now we compare the fitting of microwave transitions obtained by us with those available earlier and based on representation of the effective Hamiltonian operator in the form of a finite Taylor series in angular momentum components in the reduced Watson formulation. The first column of differences between calculated and experimental microwave frequencies in Table II corresponds to the analysis performed in this paper. The second difference column corresponds to the analysis of microwave and ir data performed in Refs. (16, 11). It should be noted here that authors of papers (16, 11) do not provide theoretical analogs of experimental data. Thus, we were able to use only theoretical values of energy levels of Ref. (16) with a rounding-off error of about 3 MHz. The differences between theory and experiment calculated on the basis of these energy levels for all microwave transitions used in fitting (16, 11) lie within the limits of this round-off error which exceeds the accuracy of measuring their frequencies on the average by several orders of magnitude. Thus, any incorrectness of the fitting in Refs. (16, 11) manifests itself explicitly only for those microwave transitions, which (i) were not used in this fitting, and (ii) can be calculated using theoretical values of energy levels available in Ref. (16). We have two such transitions only, for which we indicated differences in the second column of Table II. The Hamiltonian operator in Refs. (16, 11) contains 23 spectroscopic constants distributed by their infinitesimal orders in the following way: quadratic—3 (of 3 possible), quartic—5 (of 5), sextic—7 (of 7), octic—6 (of 9) and dectic—2 (of 11). Such a reduction of the number of higher-order constants does not have any physical basis and is in fact a forced one. The fact is, as is easy to see from the second difference column in Table II, the fitting performed in Refs. (16, 11) is not a good one compared to the accuracy of the microwave experiment. It turns out here that the introduction of a complete set of octic and dectic constants does not improve this fitting, though the total number of constants increases to 35, while their definability decreases sharply. An introduction of constants of further infinitesimal orders makes the situation even worse, i.e., the fitting of the spectrum is not improved, while the number of constants increases very sharply. Therefore the authors of Refs. (16, 11) gave up the attempt to fit the $H_2{}^{16}O$ rotational spectrum adequately and reduced the number of octic and dectic constants to improve correctness of the inverse problem. The Hamiltonian operator in paper (17), compared with papers (16, 11), possesses additionally two octic constants, one dectic constant, and one duodectic constant. As a result, the ir data of paper (13) were fitted well. Microwave data were not included in the treatment, since this might lead to a very bad fitting of both microwave and ir data. The third difference column of Table II illustrates this fact clearly. It is constructed on the basis of the prediction of microwave transitions in Ref. (17). At the same time, our treatment permitted to fit microwave transitions of $H_2{}^{16}O$ in the ground state with a mean deviation between calculation and experiment 1.2 times less than experimental uncertainty (see the first difference column in Table II). Table V displays quadratic spectroscopic constants obtained by us on the basis of the Pade operator constants of Table IV and quadratic constants of papers (16, 11) and (17). It can be easily seen that they are not in poor agreement. It should be noted that some phenomenological parameters of the Pade operator in Table IV are poorly defined and it is possible in principle to decrease the number of parameters when fitting the set of experimental data available. However, this decrease is an ambiguous one and we do not have any

TABLE V

Quadratic Spectroscopic Constants for $H_2^{16}O$ in the Ground State

	Present work	Ref. (16,11)	Ref. (17)
A	835 839.89(32)	835 840.29(50)	835 839.35(435)
B	435 354.49(42)	435 351.72(45)	435 346.73(210)
C	278 133.34(17)	278 138.70(45)	278 138.54(210)

physical grounds to prefer one of the variants of its performance. Thus we do not consider the possibility of decreasing the number of parameters in the Pade operator.

4. DISCUSSION

Since a consistent theory of construction of effective Pade Hamiltonian operators is not available, a number of questions arising in their application are still unsolved. First of all, there is much ambiguity in choosing the form of Pade operators. There are also unsolved questions regarding a regular method to be used in the search for a more effective version of treatment within the limits of the selected form of Pade operator, on the use of all information on the force field of the molecule contained in Pade operator constants. In spite of this fact, the given approach already enables one to solve a number of fundamental problems existing at present in treatment of vibration–rotational spectra of molecules with strong nonrigidity effects and consisting of interpretation, qualitative treatment, and prediction of spectral data. In particular, one of these problems is the creation of tables of microwave spectral lines for molecules of the type H_2X, XH_3 and XH_4, which are of considerable interest for purposes of astrophysics and atmosphere physics.

In conclusion, we would like to stress that though all papers on applications of Pade Hamiltonian operators for treatment of vibration–rotational spectra of molecules consider only nondegenerate vibrational states, this philosophy can be easily propagated to the treatment of degenerate states. It is convenient to use the symmetry theory methods for construction of operators H and h for the effective Pade Hamiltonian operator in this case.

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