

A New Approach to the Treatment of Rotational Spectra of Molecules with Small Moments of Inertia Applied to the PH_3 Molecule in the Ground State

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A new approach to the treatment of rotational spectra of molecules with small moments of inertia is considered based on a representation of the effective rotational Hamiltonian operator in the form of a Pade operator. An extended set of high-precision data on transition frequencies in the rotational spectrum of the PH_3 molecule in the ground vibrational state is analyzed. The fitting of these data within experimental error demonstrates the advantages of the new approach. Frequencies of the Q -branch forbidden transitions $|K| = 3 \leftarrow 6$, first measured in this work, represent an essential part of the data under consideration.

INTRODUCTION

It is well known that the basis for quantitative computation of rotational spectra of molecules is the perturbation theory. As a consequence the effective rotational Hamiltonian operator is usually represented as a finite Taylor series in components of the angular momentum. The main disadvantage of this treatment is the divergence of the finite Taylor series at high values of the total angular momentum. Actually, as the total angular momentum increases each term of the series increases without bounds and the increase of a term is faster the higher the order of its smallness parameter. It is clear, that for given precision of the experimental data, the values of the total angular momentum have an upper limit up to which this treatment is valid. Nowadays the situation in microwave spectroscopy is such that for a number of molecules with small moments of inertia there are experimental data which are close to or exceed this limit. Examples of such molecules are H_2X ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$), XH_3 ($X = \text{N}, \text{P}, \text{As}$), XH_4 ($X = \text{C}, \text{Si}, \text{Ge}$). A dramatic proof of this is provided by the fact that H_2X transition frequencies experimentally measured by microwave techniques are treated with the help of models whose number of phenomenological parameters almost coincides with the number of measured frequencies. Selection of molecules with small moments of inertia for quantitative description is justified by the following facts. On the one hand, nonrigidity effects are strongest for them. On the other hand, in spite of large rotational constants, microwave techniques make it possible to observe transitions with high values of the total angular momentum. In asymmetric tops this can be realized due to random coincidences of high rotational energy levels, in symmetric and spherical tops by observing Q -branch "forbidden" rotational transitions. To improve the treatment of rotational spectra of molecules

with small moments of inertia we propose to use an effective rotational Hamiltonian operator in the form of a Pade operator:

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

The H and h operators have the form of a standard Hamiltonian operator represented as a finite Taylor series and do not commute in the general case. Thus, the Pade Hamiltonian operator comprises $2n$ phenomenological constants (n for the numerator and n for the denominator). At high values of the total angular momentum the rotational energy tends to a constant. This asymptotic behavior is physically well justified. Treatment with the help of such an operator is significantly more efficient than that with the help of a standard Hamiltonian operator comprising $2n$ constants. Consider the interpretation of the Pade operator constants. For a Taylor expansion of the Pade operator all the coefficients of the infinite series are expressed in terms of the $2n$ constants of the Pade operator. From this point of view the Pade operator is a summed-up infinite Taylor series. This infinite series is convergent for any value of the angular momentum and its formal construction does not require a smallness parameter. Therefore, the available interpretation of quadratic, quartic, and sextic constants of this series can be readily used in the treatment by a Pade operator, even though there may not be any possibility of describing the spectrum representing the Hamiltonian operator in the form of a finite Taylor series. Naturally, direct interpretation of the Pade operator constants would have been better, but the present-day theory of molecular spectra cannot provide it. In spite of the apparent prospects, the Pade Hamiltonian operator has almost never been used for the treatment of microwave spectra of molecules. We know only one work of this kind (*1*), where pure inversion spectra of ammonia are treated in the ground vibrational state. This is evidently due to difficulties presented by the problem of finding eigenvalues and eigenvectors (wave functions) of the Pade operator. It is to be noted that in Ref. (*1*) the method of Pade approximation was used consistently only for the scalar part of the Hamiltonian operator, and the problem mentioned above was not solved. This resulted in an increase in the number of phenomenological constants required for the fitting of the spectrum and considerably complicated their interpretation. Nevertheless, in this work the inversion spectrum of ammonia in the ground vibrational state was for the first time fit with experimental precision. In the present paper we propose a simple and rigorous method of solving the problem of eigenvalues and eigenfunctions of the effective rotational Pade Hamiltonian operator. This approach has been successfully applied to fitting within experimental error a very extended set of high-precision transition frequencies for the rotational spectra of the phosphine molecule in the ground vibrational state. About 65% of this set of data has previously been reported (*2-6*), and 35% has been obtained for the first time in this work.

THEORY

Thus, in this paper an effective rotational Pade Hamiltonian operator in the form of Eq. (1) is used and we require a method of searching for its eigenvalues and

wave eigenfunctions. It is easy to see that the main difficulty here is the computation of the action of the operator $1/(1 + h)$ on the basis functions used for construction of the Pade operator matrix. Therefore, these functions are to be selected so that the computation of the action of $1/(1 + h)$ on them is maximally simplified. From this viewpoint eigenfunctions of the operator h are most suitable as basis functions.¹ Thus, the problem is solved in two stages. In the first stage eigenvalues and eigenfunctions of the operator h are searched for by any standard technique

$$\begin{aligned} h |\phi_{J,a}^{(h)}\rangle &= \lambda_{J,a}^{(h)} |\phi_{J,a}^{(h)}\rangle, \\ |\phi_{J,a}^{(h)}\rangle &= \sum_K C_{a,K}^{(h)} |\psi_{J,K}^{(\pm)}\rangle. \end{aligned} \quad (2)$$

Here $|\psi_{J,K}^{(\pm)}\rangle$ are conventional symmetrized wavefunctions of the rigid symmetrical top

$$\begin{aligned} |\phi_{J,K}^{(\pm)}\rangle &= \frac{1}{2^{1/2}} (\psi_{J,K} \pm \psi_{J,-K}) & K \neq 0 \\ &= \psi_{J,0} & K = 0. \end{aligned}$$

In the second stage we readily write down the energy matrix of the Pade Hamiltonian operator in the basis of the obtained h operator eigenfunctions

$$\begin{aligned} \langle \phi_{J,a'}^{(h)} | H_{\text{Pade}} | \phi_{J,a}^{(h)} \rangle &= \frac{1}{2} \left(\frac{1}{1 + \lambda_{J,a'}^{(h)}} + \frac{1}{1 + \lambda_{J,a}^{(h)}} \right) \langle \phi_{J,a'}^{(h)} | H | \phi_{J,a}^{(h)} \rangle \\ &= \sum_{K,K'} T_{a'a,K'K}^{(h)} \langle \psi_{J,K'}^{(\pm)} | H | \psi_{J,K}^{(\pm)} \rangle, \end{aligned} \quad (3)$$

where

$$T_{a'a,K'K}^{(h)} = \frac{1}{2} C_{a'K'}^{(h)*} C_{aK}^{(h)} \left(\frac{1}{1 + \lambda_{J,a'}^{(h)}} + \frac{1}{1 + \lambda_{J,a}^{(h)}} \right). \quad (4)$$

The discussion below is given for the treatment of the transition frequencies of the rotational spectrum of the PH_3 molecule in the ground vibrational state.

Using the methods of the symmetry theory (6, 7) we can obtain the scheme of rotational levels in the Born–Oppenheimer approximation for the phosphine molecule ground state displayed in Fig. 1. The splittings seen in this scheme are due to the effects of K doubling and inversion motion. Note that inversion splitting in PH_3 is very small and has not been detected experimentally. Its most stringent upper limit in the ground state of PH_3 has been obtained in Ref. (6). To describe transition frequencies in the ground state of phosphine taking into account effects of K doubling and inversion splitting, a Pade Hamiltonian operator is used with an H operator in the form

$$\begin{aligned} H = & BP^2 + (C - B)P_z^2 - D_J P^4 - D_{JK} P^2 P_z^2 - D_K P_z^4 + H_J P^6 + H_{JJK} P^4 P_z^2 \\ & + H_{JKK} P^2 P_z^4 + H_K P_z^6 + (1/2)\Delta_3(P_+^6 + P_-^6) \pm \Delta_i, \end{aligned} \quad (5)$$

¹ Eigenfunctions of the rigid symmetric top commonly used as basis functions for construction of the Hamiltonian operator matrix do not hold here.

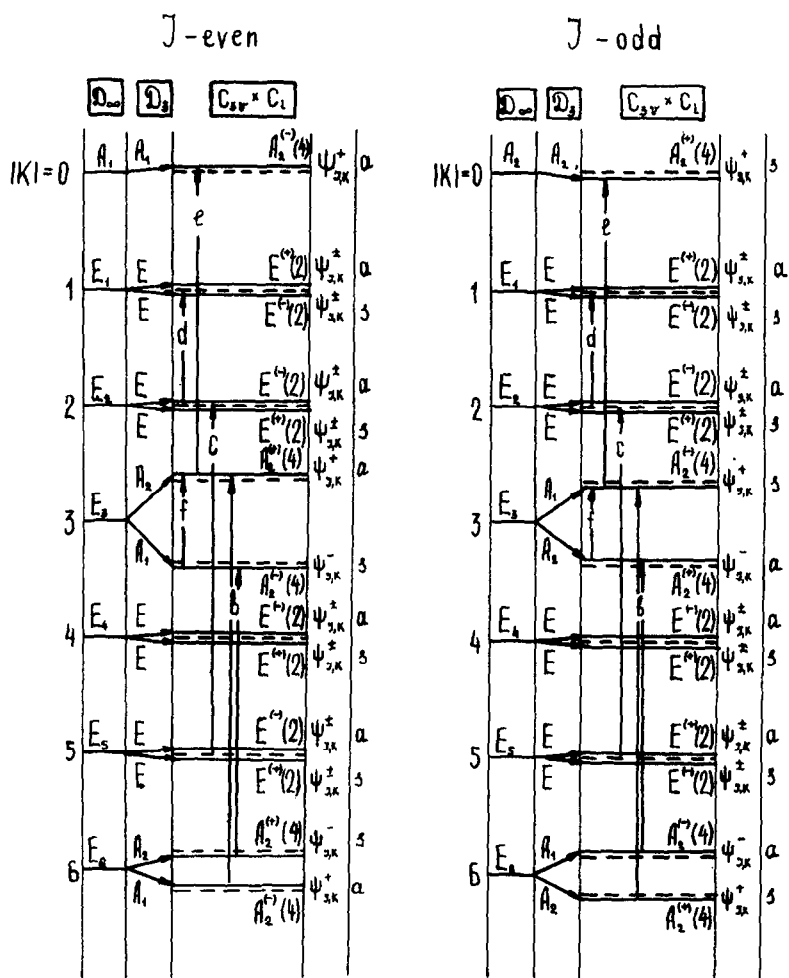


FIG. 1. Diagram of rotational levels of the PH_3 molecule in the ground state, shown under the assumption that the splitting due to K doubling significantly exceeds inversion splitting. D_∞ is the symmetry group in the rigid-top approximation. $C_{3v} \times C_i$ is the symmetry group in the Born-Oppenheimer approximation. Figures in brackets following the multiplet legends are nuclear statistical weights. Broken lines show the positions of the levels when inversion splitting is neglected. Arrows show the experimentally observed Q -branch transitions; their legends correspond to those in Table I. D_3 is the rotational subgroup matching the symmetry groups of the rigid-top and Born-Oppenheimer approximations. Symmetrized wave functions of the rigid symmetric top ψ_{JK}^\pm are considered in the basis where one of the reflection planes of the C_{3v} group coincides with the coordinate plane XZ (Z is the molecule axis of symmetry).

where P , P_z are the operators of the total angular momentum and its component along the molecule symmetry axis, respectively; $P_\pm = P_x \pm iP_y$; Δ_i is the inversion splitting constant. Correspondingly, the h operator has the form

$$h = bP^2 + (c - b)P_z^2 - d_J P^4 - d_{JK} P^2 P_z^2 - d_K P_z^4 + h_J P^6 + h_{JK} P^4 P_z^2 + h_{KK} P^2 P_z^4 + h_K P_z^6 + (1/2)\delta_3(P_+^6 + P_-^6). \quad (6)$$

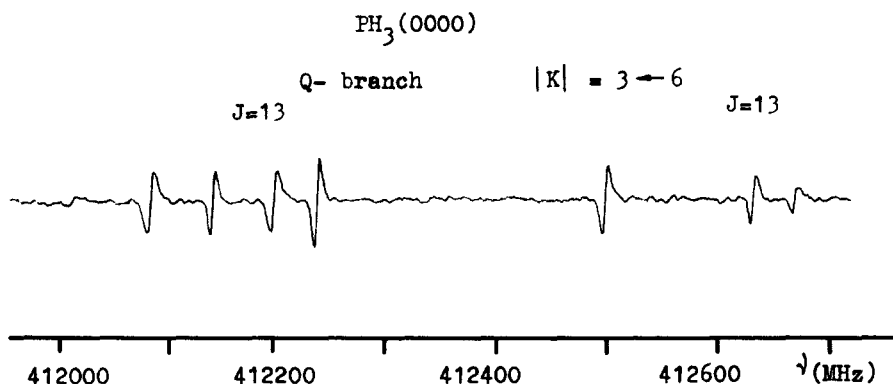


FIG. 2. Part of the absorption spectrum of the PH_3 molecule containing the Q -branch forbidden transition $|K| = 3 \leftarrow 6$ with $J = 13$. Due to the effect of K doubling the transition is observed as a doublet with components of equal intensity. The spectrum was recorded for a chemically pure phosphine sample at a pressure $P = 0.4$ Torr and temperature $T = 293$ K. Absorption lines at the frequencies 412 084.15, 412 198.52, 412 236.88, 412 495.50, and 412 664.18 MHz are not identified. All the spectral lines are recorded as the first derivative of their absorption profile.

Consequently, our Pade Hamiltonian operator contains a maximum of 21 phenomenological constants.

EXPERIMENTAL DETAILS

The rotational spectrum of the phosphine molecule in the ground vibrational state was investigated with the help of the submillimeter microwave spectrometer RAD (8) and the submillimeter frequency synthesizer (SFS) (9). The SFS range was expanded up to 840 GHz as compared to the previous study (6). All the investigations were carried out at room temperature. The frequencies of the Q -branch forbidden transitions $|K| = 3 \leftarrow 6$ with a doublet structure due to the effect of K doubling were observed and measured for the first time. In addition, the frequencies of the R -branch allowed transitions $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ were measured with a precision more than one order of magnitude better as compared to Refs. (2) and (6), respectively. A part of the PH_3 spectrum with the Q -branch forbidden transitions $|K| = 3 \leftarrow 6$ is shown in Fig. 2.

Tuning to the center of the absorption line when measuring its frequency was accomplished with the help of the automatic frequency control (AFC) with the first derivative of the line profile as a reference. The results of the measurements are presented in Table I together with the previously known experimental data (2–6) on transition frequencies in the rotational spectrum of PH_3 in the ground vibrational state. The main source of errors in measuring high-intensity allowed transitions is the shift of the transition frequencies due to pressure. Therefore, values of the frequencies for these transitions were determined for zero pressure by the extrapolating results of measurements at several values of the pressure in the absorption cell (see Fig. 3). All the frequencies of the Q -branch forbidden transitions $|K| = 3 \leftarrow 6$ given in Table I correspond to the pressure in the absorption cell $P \sim 0.4$ Torr.

TABLE I
Measured and Calculated Frequencies of Rotational Transitions for the PH₃
Molecule in Its Ground Vibrational State

Transition	Meas. Freq. (MHz)	Calc. Freq. (MHz)	$\nu_m - \nu_c$ (KHz)	$\nu_m - \nu_c^*$ (KHz)
	ν_m ($h\nu_m$)	ν_c ($h\nu_c$)		
Allowed Rotational Transitions				
$J+1 \leftarrow J$ $K \leftarrow K$				
J=0 K=0	266 944.520(40) ^a	266 944.511(12)	9	0
1 0	533 794.595(10) ^b	533 794.593(7)	2	-10 ⁺
1 1	533 815.244(10)	533 815.247(7)	-3	10 ⁺
2 0	800 456.200(10)	800 456.196(7)	4	80 ⁺
2 1	800 487.090(10)	800 487.090(6)	0	-70 ⁺
2 2	800 579.896(10)	800 579.901(7)	-5	10 ⁺
3 0	1 066 835.85(20) ^a	1 066 835.935(99)	-85	-60
3 1	1 066 876.90(20)	1 066 876.966(99)	-66	-80
3 2	1 067 000.33(20)	1 067 000.227(99)	103	50
3 3	1 067 206.26(20)	1 067 206.200(99)	60	80
Forbidden Rotational Transitions				
$J \leftarrow J$ $K \leftarrow K+1 \leftarrow K+2$				
J=6	47 391.16(56) ^d	47 390.444(20)	716	240
7	47 178.66(36)	47 178.723(20)	-63	-450
8	46 939.04(24)	46 938.810(20)	230	-50
9	46 671.48(16)	46 671.515(20)	-35	-198
10	46 377.80(24)	46 377.739(20)	61	22
11	46 058.52(12)	46 058.475(19)	45	129
12	45 714.84(20)	45 714.796(19)	44	229
13	45 347.84(24)	45 347.852(23)	-12	220
14	44 958.68(28)	44 958.846(32)	-166	-10
15	44 548.88(24)	44 549.013(49)	-133	-290
16	44 119.80(52)	44 119.563(82)	237	-690
17	43 671.08(56)	43 671.61(15)	-532	-3080
$J \leftarrow J$ $ K \leftarrow 0 \leftarrow 2$				
J=3	143 701.63(10) ^e	143 701.565(61)	65	82
4	143 331.01(10)	143 331.085(50)	-75	-75
5	142 869.93(10)	142 869.906(43)	24	13
6	142 319.00(10)	142 318.958(42)	40	29
7	142 679.05(10)	141 679.013(39)	37	32
8	140 950.44(10)	140 950.496(40)	-56	-48
9	140 133.10(10)	140 133.279(42)	-179	-158
10	139 226.51(10)	139 226.437(43)	73	97
11	138 228.01(10)	138 227.992(42)	18	26
12	137 134.66(10)	137 134.631(43)	29	6
13	135 941.42(10)	135 941.405(52)	15	-28
14	134 641.42(10)	134 641.420(73)	0	24
$J \leftarrow J$ $ K \leftarrow 2 \leftarrow 5$				
J=6	333 839.95(15) ^c	333 839.754(92)	196	-210
7	332 344.95(15)	332 345.236(76)	-286	-440
8	330 651.65(15)	330 651.590(66)	60	150
9	328 764.43(15)	328 764.482(59)	-52	230
10	326 690.32(15)	326 690.241(57)	79	470
11	324 435.91(15)	324 435.855(59)	55	410
12	322 008.98(15)	322 008.980(66)	0	150
13	319 417.85(15)	319 417.950(73)	-100	-300
14	316 671.85(15)	316 671.830(77)	20	-530
15	313 780.44(15)	313 780.496(79)	-56	-570
16	310 754.78(15)	310 754.79(13)	-10	650
$J \leftarrow J$ $ K \leftarrow 3 \leftarrow 6$ $t \leftarrow t$				
J=7 t=s	429 108.40(10) ^b	429 108.509(60)	-109	
7 a	429 095.60(10)	429 095.540(60)	60	
8 a	426 926.61(10)	426 926.603(39)	7	
8 s	426 898.13(10)	426 898.120(39)	10	
9 s	424 500.85(10)	424 500.856(38)	-6	
9 a	424 444.06(10)	424 444.000(38)	60	
10 a	421 843.01(10)	421 843.031(39)	-21	
10 s	421 737.71(10)	421 737.663(39)	47	
11 s	418 967.07(10)	418 967.062(38)	8	
11 a	418 783.13(10)	418 783.087(37)	43	
12 a	415 889.32(10)	415 889.327(37)	-7	
12 s	415 583.29(10)	415 583.447(36)	-157	
13 s	412 628.90(10)	412 628.952(40)	-52	
13 a	412 140.82(10)	412 140.798(40)	22	
14 a	409 208.22(10)	409 208.141(42)	79	
14 s	408 455.72(10)	408 455.742(49)	-22	
15 s	405 652.65(10)	405 652.551(46)	99	
15 a	404 527.02(10)	404 527.071(54)	-51	
16 a	401 991.65(10)	401 991.706(75)	-66	
16 s	400 351.39(10)	400 351.399(57)	-9	
17 a	395 922.75(10)	395 922.781(67)	-31	
18 a	394 494.56(10)	394 494.586(99)	-26	
18 s	391 232.31(10)	391 232.318(94)	-8	
Molecular Beam Resonance Transitions				
$ K \leftarrow 3$ splitting				
J=3	0.062 25(20) ^f	0.062 057(3)	0.193	0.192
4	0.434 09(20)	0.434 011(14)	0.079	0.070
5	1.734 13(20)	1.734 131(40)	-0.001	-0.024
6	5.195 70(20)	5.195 551(83)	0.149	0.120
7	12.969 00(20)	12.969 07(13)	-0.070	-0.080
8	28.482 50(20)	28.482 54(14)	-0.040	0
9	56.855 00(20)	56.854 94(20)	0.060	0.010

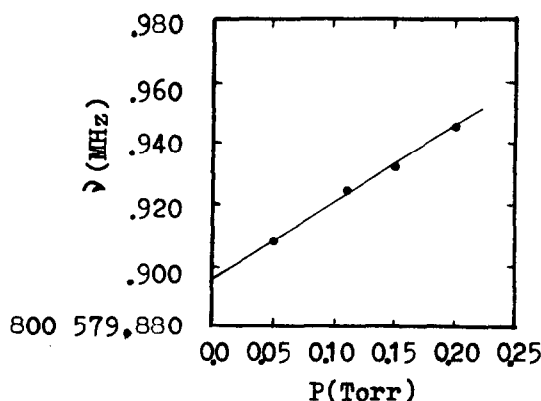


FIG. 3. Pressure dependence of the transition frequency $J = 3 \leftarrow 2$, $K = 2$ of the phosphine molecule in the ground vibrational state. The value of the shift due to pressure determined by this dependence equals 245 KHz/Torr.

The measurement error of these transition frequencies was determined mainly by the signal-to-noise ratio. The indicated error is somewhat exaggerated to allow for a possible frequency shift due to pressure which was not determined for the forbidden transitions.

ANALYSIS

All the known experimental data (see Table I) on the absorption line frequencies of the phosphine molecule in the ground vibrational state were used in the fitting. The algorithm used for solving the inverse spectroscopic problem was described in Ref. (8). As in the previous paper (6) we were unable to determine in a least-squares sense the constant of the inversion splitting Δ_i , namely,

$$\Delta_i = 3.8(400) \text{ Hz.}$$

A slight improvement of the upper limit Δ_i as compared to Ref. (6) is due to the following reasons: (i) expansion of the set of experimental data; (ii) consideration of the influence of inversion splitting on all the experimentally measured transitions unlike in Ref. (6), where its effect is taken into account only for transitions between K -doublet states with $|K| = 3$. Since the inversion splitting constant cannot be determined and, practically, does not correlate with the other

* The difference column between theory and experiment corresponding to the analysis carried out in Ref. (6).

† Precision of measurements of the allowed transition frequencies $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ in Ref. (6) was more than one order of magnitude worse.

^a Helminger and Gordy (2).

^b The present paper.

^c Belov *et al.* (6); in the present paper the measurement error given in Ref. (6) for the branch $|K| = 2 \leftarrow 5$ is corrected (see the text).

^d Chu and Oka (4).

^e Helms and Gordy (5).

^f Davis *et al.* (3).

TABLE II—Continued

[illegible]

paper, the value of this error is in accordance with the characteristics of the apparatus used in Ref. (6).

(iii) A very good description of the forbidden transition Q -branch $|K| = 3 \leftarrow 6$ is given. Experimental data for this branch are obtained in the present paper. Attempts to treat all the experimental data according to Ref. (6) resulted in deterioration of the fitting. We could have increased the number of the terms in the Taylor series, of course, but even the taking account of terms of the next order of smallness (of 10th degree in components of the angular momentum) requires introduction of 6 additional phenomenological constants. We have, in fact, to consider terms of the 12th degree in components of the angular momentum. This follows from Table III, where results of the computation (based on the constant from Table II) are presented for the levels with $|K| = 6$ which are split due to K -doubling effects. It is clear, that a consideration of the split levels with $|K| = 6$ is necessary for proper fitting of the experimental data for the forbidden transition branch $|K| = 3 \leftarrow 6$. The first constant³ independent of Δ_3 and leading to the splitting, however, stands in the Taylor series before the term of 12th degree in components of the angular momentum.

One more feature is also of interest. At first we were not planning to remeasure the previously measured (2, 6) frequencies of the allowed transitions. The treatment of the available experimental data based on the Pade Hamiltonian operator resulted, however, in significant deterioration of the fitting of the allowed transition frequencies as compared to the traditional treatment (6). Disagreement be-

³ This constant is required, in the first place, for fitting of the split levels with $|K| = 3$.

TABLE III

Results of Computation of the Level Splitting with $|K| = 6$ due to K Doubling for the PH_3 Molecule in Its Ground Vibrational State

J	ΔE (KHz)	J	ΔE (KHz)
6	0.003 0843 (11)	13	157.635(47)
7	0.040 148 (14)	14	395.22 (12)
8	0.281 491 (96)	15	924.98 (26)
9	1.410 04 (47)	16	2041.50 (54)
10	5.651 8 (18)	17	4283.0 (11)
11	19.259 6 (61)	18	8595.9 (21)
12	57.921 (18)		

tween calculation and experiment (250 KHz instead of the formerly available 10 KHz obtained previously from the traditional treatment) was most substantial for the transitions $J = 2 \leftarrow 1$. To ascertain the cause of such deterioration of the fitting we remeasured the transition frequencies for $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ with a precision more than one order of magnitude better. From Table I it is clear that the new measurements of the allowed transitions are in good agreement with the treatment based on the Pade operator, that is, the disagreement was due to poor accuracy of the previous measurements. Thus, the new approach made it possible to reveal that the experimental error for allowed transitions was really as large as indicated in Ref. (2). This fact was not observed in the traditional treatment. This is explained by the following. When the Hamiltonian operator is represented as a Taylor series, fitting of allowed and forbidden transitions takes place almost independently. The number of measured allowed transitions is small, therefore their fitting is, naturally, much better than the actual measurement error. In the treatment with the help of a Pade Hamiltonian operator all the constants are used for fitting both allowed and forbidden transitions. Therefore, different types of transitions contribute to the fitting of one another. In our opinion, this means better physical adequacy of the proposed model compared to the traditional one.

It is to be noted that many phenomenological constants of the Pade operator in Table II are poorly defined and in the fitting of the available experimental data their number may be decreased. Up to four constants may be excluded practically without deterioration of the fitting. This exclusion, however, is ambiguous and we have no physical grounds in favor of a certain version. Therefore, we did not attempt to decrease the number of Pade operator constants. It should be emphasized that prediction of the spectrum in a new frequency region as well as the transition from the phenomenological Pade operator constants to the Taylor series is readily accomplished using all the constants from Table II. One must only bear in mind that in the estimation of the precision of the spectrum prediction and the precision of determination of spectroscopic constants, the principal role belongs to the matrix of correlation coefficients for the Pade operator constants. As an example the quartic spectroscopic constants D_K^{Sp} , D_K^{Sp} , and D_K^{Sp} are given below calculated on the basis of the Pade operator constants from

Table II:

$$D_J^{Sp} = D_J + Bb = 3938.8(18) \text{ KHz},$$

$$D_{JK}^{Sp} = D_{JK} + (C - B)b + B(c - b) = -5173.52(40) \text{ KHz},$$

$$D_K^{Sp} = D_K + (C - B)(c - b) = 4240.9(13) \text{ KHz}.$$

These values of the quartic spectroscopic constants are significantly more precise than those obtained in Ref. (6). We believe that this is due not only to an increase of the number of available experimental data but to a better physical adequacy of the proposed model. Generally speaking, in a similar way we can obtain spectroscopic constants of a very high order of smallness. The only limit here is the gradual deterioration of the relative precision of spectroscopic constants with the increase of their order of smallness.

SUMMARY

This paper demonstrates the advantages of a treatment of molecular spectra with small moments of inertia based on a representation of the effective Hamiltonian operator in the form of a Pade operator. This, in our opinion, proves that the proposed model is physically more adequate than the traditional treatment. It is to be noted that based on this approach we have treated (10) the available experimental data (11) on the frequencies of the H_2S rotational transitions in the ground vibrational state. As compared to the traditional treatment (11) our results are about 450 times better (in units of measurement error) for the same number of model parameters. The frequencies of the rotational transitions of H_2X -type molecules have thus for the first time been described within the limits of their experimental error. We hope that the approach described will make it possible to solve a number of basic problems in the treatment of molecular spectra with small moments of inertia concerning interpretation, quantitative description, and prediction of these spectra.

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