On determination of equilibrium structure parameters of PH_3 molecule

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A method is proposed for determination of equilibrium structure parameters of the PH_3 molecule from only experimental data (without any assumptions on the model of a molecule).

One of the most important problems of spectroscopy is determination of the correct equilibrium structure of molecules, because it is one of the central points in solution of almost any theoretical or applied problem of molecular physics. In this paper, we consider this problem as applied to the PH_3 molecule, the spectroscopic information about which is necessary for solving numerous problems of atmospheric optics and astrophysics.

Earlier the problems connected with determination of the equilibrium structure of this molecule (r_e P–H and α_e – the angle between the P–H bonds) were considered in Refs. 1–5. However, it should be noted that in Refs. 1–3 the result was obtained from analysis of microwave data (i.e., the case in point is a determination of the so-called structure of the ground state, rather than equilibrium parameters r_e and α_e). In Ref. 5, the parameters were determined from *ab initio* calculations, in which case the results of calculation with different basis functions differ quite strongly.

In Ref. 4, the parameters r_e and α_e were determined from analysis of four fundamental bands of the PD_3 molecule. However, because of the presence of resonances in that case, the resonance constants had to be estimated numerically. This naturally invoked the information on the model of the molecule (in particular, parameters of the potential function).

This circumstance, in its turn, does not allow us to assert that the obtained result is correct, because the changes in the model used in calculations necessarily lead to a change of the final result.

At the same time, the procedure proposed and implemented in this work allows the parameters r_e and α_e to be determined from only experimental data without any assumptions on the parameters of the potential function, resonance constants, etc. In this case, we used high-resolution spectra of 12 fundamental bands of the PH_2D and PHD_2 molecules as the initial data.

To explain the essence of our approach, remind that three rotational constants of some or other vibrational state ($v_1 \ldots v_n$) (here n is the number of vibrational modes) of an asymmetric top molecule are determined by the equation

$$A_\beta^{v_1 \ldots v_n} = A_\beta^e - \sum_\lambda \alpha_\lambda^\beta \left(v + \frac{1}{2} \right), \qquad (1)$$

where A_β^e are the corresponding rotational constants for the equilibrium configuration of nuclei in the molecule; α_λ^β are rotational-vibrational coefficients; $\beta = x$, y, or z; $A_z = A$; $A_x = B$, and $A_y = C$.

From Eq. (1) it directly follows that

$$A_\beta^e = \frac{n+2}{2} A_\beta^{gr} - \frac{1}{2} \sum_{\lambda=1}^{n} A_\beta^{v_\lambda=1}, \qquad (2)$$

where $A_\beta^{v_\lambda=1}$ denotes the A_β-parameters for the corresponding single-excited vibrational states ($\ldots v_\lambda \ldots$); A_β^{gr} are the rotational constants of the ground vibrational state. It is seen from Eq. (2) that, to determine correctly the equilibrium parameter A_β^e, one should know: (a) the values of the corresponding rotational constants of the ground vibrational states (in our case, these parameters can be taken from Ref. 6), (b) the values of rotational constants of absolutely all single-excited vibrational states $A_\beta^{v_\lambda=1}$.

Note that the problem of correct determination of the latter although looks simple at first glance, is not actually simple, because in the presence of resonance interactions (which can be rather strong), the spectroscopic parameters of resonating bands correlate to some or other degree, and the values of rotational constants, found from solution of the inverse problem, may depend strongly on specific values of resonance parameters (the number of these resonance parameters may be large). Under these conditions, choosing between possible sets of parameters obtained from different solutions of the inverse problem is a nontrivial problem. One of the ways to solve it is to estimate resonance parameters based on numerical simulation of the molecular structure and potential function. Naturally, this way cannot be considered as fully correct, because the result turns to be directly dependent on the used model, and it obviously changes as the model changes.

Assume that we know the experimental values of the rotational-vibrational energy levels for $J = 0$ and 1 (i.e., E_{000}, E_{101}, E_{111}, and E_{110}) for all single-excited states of the molecule. Keeping in mind that the sum of roots of any secular equation is equal to the sum of diagonal elements of the corresponding matrix and

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independent of its off-diagonal elements (i.e., in our case, any matrix elements dependent on resonance parameters), we can see that $\sum_{\lambda=1}^{n}\sum_{\beta} A_{\beta}^{v_\lambda=1}$ (the sum of all three rotational constants of all single-excited states) is a constant independent of the particular value of any one of resonance parameters used for determination of rotational constants from experimental data. What's more, the accuracy of determination of $\sum_{\lambda=1}^{n}\sum_{\beta} A_{\beta}^{v_\lambda=1}$ depends only on the accuracy of experimental data.

In practical solving of the problem, as the initial data we used the values of energy levels for $J \le 2$ obtained from the analysis of experimentally recorded spectra of all fundamental bands of the PH_2D and PHD_2 molecules. The experimental spectra have been recorded on the IFS 120HR Fourier transform spectrometer of the University of Wuppertal, Germany (for details see Ref. 7). The corresponding "experimental" energy levels are tabulated in Tables 1 and 2.

Using Eq. (2), we can readily obtain $S = \sum_{\beta} A_{\beta}^{e}$ for both PH_2D and PHD_2: $S_{PH_2D} = (10.207222 \pm \pm 0.000073)$ cm^{-1} and $S_{PHD_2} = (8.0913 \pm 0.0030)$ cm^{-1}. It should be noted here that in spite of the high accuracy of experimental line positions (no less than 0.0001 cm^{-1}), the confidence interval for S_{PH_2O} more than 20 times exceeds the experimental accuracy. This is a consequence of the fact that the dyad of the states $(v_2 = 1)/(v_5 = 1)$ of the PHD_2 molecule is in a strong resonance with the vibrational state $(v_3 = v_4 = 1)$.

As our analysis shows, the influence of this state on the rotational constants of the states $(v_2 = 1)$ and $(v_5 = 1)$ and, consequently, on $\frac{1}{2}\sum_{\lambda=1}^{n}\sum_{\beta} A_{\beta}^{v_\lambda=1}$, which is used to determine the sum $(A_e^{exper.} + B_e^{exper.} + C_e^{exper.})$, is not small and achieves the value indicated in the confidence interval. As a consequence, a more correct result can be obtained only with all experimental data on all double-excited vibrational states in hand, but this problem hardly can be solved nowadays.

At the same time, it is well-known that

$$A^e + B^e + C^e = \frac{h}{8\pi^2 c}\left(\frac{1}{I_A^e} + \frac{1}{I_B^e} + \frac{1}{I_C^e}\right), \qquad (3)$$

where I_A^e, I_B^e, and I_C^e are equilibrium inertia moments, which can be easily related to the structure parameters r_e and α_e. As a result, $r_e = (1.416776 \pm 0.000164)$ Å and $\alpha_e = (93.56 \pm 0.29)°$.

Table 1. "Experimental" rotational-vibrational energy levels of fundamental bands of the PH_2D molecule

J	K_a	K_c	$v_1 = 1$	$v_2 = 1$	$v_3 = 1$	$v_4 = 1$	$v_5 = 1$	$v_6 = 1$
0	0	0	2322.40433	1688.51225	1093.57114	891.91335	2326.42983	969.48071
1	0	1	2329.64440	1695.78603	1100.92421	899.05788	2336.68070	976.98088
1	1	1	2329.44512	1695.59846	1100.71625	898.93830	2333.49323	976.68249
1	1	0	2328.14511	1694.21151	1099.48596	897.60166	2332.17155	975.17088
2	0	2	2345.24866	1711.55563	1116.67457	914.57266	2349.33313	993.22867
2	1	2	2345.21187	1711.53755	1116.65076	914.56513	2349.31490	993.18872
2	1	1	2341.32327	1707.37612	1112.95994	910.55333	2345.36312	988.65754
2	2	1	2340.72549	1706.80517	1112.33571	910.19411	2344.78389	987.76322
2	2	0	2339.60447	1705.59056	1111.28936	908.97019	2343.63451	986.51104

Note. All the values are given in cm^{-1}.

Table 2. "Experimental" rotational-vibrational energy levels of fundamental bands of the PHD_2 molecule

J	K_a	K_c	$v_1 = 1$	$v_2 = 1$	$v_3 = 1$	$v_4 = 1$	$v_5 = 1$	$v_6 = 1$
0	0	0	2324.00483		911.65192			978.55875
1	0	1	2328.87950	1690.92723	916.44613	771.75390	1697.64070	983.58766
1	1	1	2329.26756	1691.34350	916.86951	772.14731	1698.01997	983.96798
1	1	0	2329.81560	1691.92929	917.55940	772.72089	1698.58980	984.44320
2	0	2	2338.32305	1700.28823	925.62633	781.16173	1707.06676	993.39296
2	1	2	2338.46844	1700.44349	925.76968	781.30618	1707.20572	993.54806
2	1	1	2340.11196	1702.19806	927.83662	783.02653	1708.91414	994.97531
2	2	1	2341.27562	1703.44616	929.10616	784.20638	1710.05108	996.11594
2	2	0	2341.58061	1703.76955	929.51591	784.53063	1710.37777	996.36517

Note. All the values are given in cm^{-1}.

Table 3. Equilibrium structure parameters and equilibrium rotational constants of the PHD_2 and PH_2D molecules

Reference	r_e, Å	α_e, deg	$S^e_{PH_2D}$, cm^{-1}	$S^e_{PHD_2}$, cm^{-1}
1	1.41154	93.36	10.282270	8.152924
2	1.41159	93.328	10.281434	8.152536
3	1.413	93.45	10.261350	8.135546
4	1.41175	93.421	10.279425	8.150134
5*	1.41105	93.497	10.289907	8.157761
5**	1.418453	93.5139	10.182843	8.072729
Our data	1.416776 ±0.000164	93.56±0.29	10.20722	8.0913
Experiment			10.20722	8.0913

* *Ab initio* calculations based on cc-pwCVQZ basis functions (for details see Ref. 5).

** *Ab initio* calculations based on cc-pVTZ basis functions.

In this connection, it is interesting to compare the calculated results on S_{PH_2D} and S_{PHD_2} with different sets of the parameters r_e and α_e known in the literature. The results of such a comparison are given in Table 3. From the above description of the procedure of determination of the parameters r_e and α_e it is obvious that in our case the values of S_{PH_2D} and S_{PHD_2} are exact. At the same time, any other set of parameters gives a difference with the corresponding "experimental" values, and this difference far exceeds the experimental accuracy.

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