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Isotopic Effects in XH_3 (C_{3v}) Molecules: The Lowest Vibrational Bands of PH_2D Reinvestigated

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We have derived, for ${}^{M}X^{m}Y_3$ (C_{3v} symmetry) molecules which satisfy the conditions of a small ratio of atomic masses m_H/m_X and of equilibrium angles Y–X–Y close to $\pi/2$, simple isotopic relations for rotation–vibration parameters α_λ^β for the case where one light atom Y (=H) is replaced by a heavier one (=D). The usefulness and predictive power of such relations for the assignment and in the fit were tested by analyzing novel high resolution Fourier transform spectra of the PH_2D molecule. The region of the three lowest-lying vibrational–rotational bands ν_4, ν_6, and ν_3 was studied. The accurate analysis was made possible with the help of recently obtained (O. N. Ulenikov, H. Bürger, W. Jerzembeck, G. A. Onopenko, E. S. Bekhtereva, and O. L. Petrunina, *J. Mol. Struct.*, in press) precise rotational energies of the ground vibrational state of PH_2D. This improvement, in conjunction with better resolution and higher sensitivity, enabled us to assign transitions with higher values of quantum numbers J and K_c and to obtain more accurate rotation–vibration energies of upper states than previously. These energies, fitted with a Watson-type Hamiltonian in A reduction and III^l representation, lead to a physically meaningful set of spectroscopic parameters which reproduce the experimental energies with a precision close to experimental uncertainty. Agreement between predicted and fitted Coriolis and vibrotational constants is noted; apparent limitations are caused by significant deviation of PH_3 and PH_2D from the idealized local mode case model.

Key Words: vibration–rotation spectra; PH_2D molecule; spectroscopic parameters.

1. INTRODUCTION

In recent contributions (*1, 2*) we derived and discussed sets of simple isotopic relations which connect spectroscopic parameters of near-local-mode molecules XH_2 (C_{2v}) and their substituted XD_2 (C_{2v}) and XHD (C_i) species. The predictions derived by relations show impressively high predictive power when compared with the results of analysis of experimental vibration–rotation spectra of the D_2Se and HDSe molecules. In continuation of this work, the present contribution is devoted to the analysis of the analogous problem relating XH_3 (C_{3v}) and XH_2D (C_s) molecules. Here XH_3 is an axially symmetric, 4-atomic molecule which we call a "near-local-mode molecule" if it satisfies the conditions

(a) the ratio of atomic masses m_H/M_X is small;
(b) the equilibrium angle H–X–H is close to $\pi/2$;
(c) the X–H stretching frequencies are very close to each other and considerably larger than the bending frequencies.

In the present study, the PH_2D molecule is used as a test case for the derived theoretical results. The study of high-resolution vibration–rotation spectra of the PH_3 molecule and its isotopic species is a project of general interest. On the one hand, phosphine plays an important role in astrophysics and planetology (see, e.g., Refs. (*3–5*), and references therein), which generates large interest in laboratory spectroscopic investigations of this molecule. On the other hand, the phosphine molecule is one of the lightest and simplest symmetric top molecules. Hence spectroscopic effects and peculiarities inherent to symmetric tops should be particularly pronounced in its spectra. Moreover, in our opinion PH_3 and its different isotopic species can be considered as test cases to examine the validity and accuracy of different theoretical approaches, in particular those commonly used for modeling isotopic substitution effects in XH_3 molecules which satisfy the above mentioned conditions (a)–(c).

Extensive studies of PH_3 spectra have been performed in the infrared region (see (*6–8*) and references cited therein). To the contrary, there are only two contributions devoted to the analysis of infrared spectra of the PH_2D species: the bands $\nu_2(a')$, $\nu_3(a')$, $\nu_4(a')$, and $\nu_6(a'')$ [ν_{3a}, ν_{4a}, ν_2, and ν_{4b} in the notation of Refs. (*9, 10*)] have been investigated, and an interaction model involving Coriolis resonances between ν_3, ν_4 and ν_6 has been established (*10*). As was mentioned in our earlier work (*11*), we have recorded high-resolution spectra of the PH_2D molecule in the wide spectral region from 20 to 5000 cm^{-1}. Having analyzed the far infrared, pure rotational part of the recorded spectrum, we felt that a reanalysis of the lowest vibrational bands due to the bending modes ν_3, ν_4, and ν_6 would be appropriate in spite of the fine previous work (*10*) for several reasons.

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First, the ground state rotational energies obtained in (*11*) are significantly more accurate than those obtained in Refs. (*9, 10*), because of the large body of more accurate data, and this is of relevance also for the excited states.

Second, the higher resolution (2.3×10^{-3} cm^{-1}, 1/maximum optical path difference) than in (*9, 10*) (5×10^{-3} cm^{-1}) and the higher signal:noise ratio of our experimental data in comparison with those of Refs. (*9, 10*) enabled us to assign weaker lines. This gave us the possibility of observing transitions with higher values of the quantum numbers J and K_c (K_a in the notation of Refs. (*9*) and (*10*)). Thereof, we were able to deduce more precise and extensive information on the rotational structure and spectroscopic parameters of the states (001000), (000100), and (000001) in the notation ($\nu_1\nu_2\nu_3\nu_4\nu_5\nu_6$).

Third, and most importantly, we use the present data on PH_2D as a test case for the relations deduced for isotopic substitution $XH_3 \rightarrow XH_2D$. This will be elaborated in Section 2 of the present contribution.

Sections 3 and 4 are devoted to a short description of the experimental details and the used Hamiltonian model. The assignment of experimental transitions and the results of the reanalysis will be discussed in Section 5.

2. ISOTOPIC SUBSTITUTION $XH_3 \rightarrow XH_2D$ IN AN XH_3 MOLECULE WITH C_{3V} SYMMETRY

From a general physical point it is obvious that a number of relations must exist between different isotopic species of molecules when they physically only differ from each other by the atomic masses. As was discussed in Ref. (*12*), the possibility of deriving such isotopic relations is mathematically based on the fact that exact connections exist between transformation coefficients $l_{N\alpha\mu}$ and $l'_{K\gamma\lambda}$ of a "mother" and a "daughter" species, respectively:

$$l'_{N\beta\lambda} = \sum_{\alpha\mu} \mathcal{K}^e_{\alpha\beta}(m_N/m'_N)^{1/2} l_{N\alpha\mu}\beta_{\lambda\mu}. \quad [1]$$

Here m_N and m'_N are the masses of the Nth atom before and after isotopic substitution, respectively. The coefficients $\beta_{\lambda\mu}$ are the elements of the matrix which is inverse to the matrix $\alpha_{\lambda\mu}$. The matrix $\alpha_{\lambda\mu}$ performs the transformation from the normal vibrational coordinates of a "mother" molecule to those of a "daughter" species. The matrix elements $\alpha_{\lambda\mu}$ are determined by (see, for details, Ref. (*12*))

$$\sum_{\nu} \alpha_{\lambda\nu}\alpha_{\mu\nu} = A_{\lambda\mu} = \sum_{N\alpha} \frac{m_N}{m'_N} l_{N\alpha\lambda} l_{N\alpha\mu}, \quad [2]$$

$$\sum_{\nu} A_{\lambda\nu} W_\nu \alpha_{\nu\mu} = \alpha_{\lambda\mu} W'_\mu \quad [3]$$

and lead to the secular equation

$$\det\{\mathbf{AW} - \mathbf{W}'\} = 0,$$

where $\mathbf{A}$ is the matrix with the elements $A_{\lambda\nu}$; $\mathbf{W}$ and $\mathbf{W}'$ are the diagonal matrices with the elements $W_{\lambda\nu} = \omega^2_\lambda \delta_{\lambda\nu}$ and $W'_{\lambda\nu} = \omega'^2 \delta_{\lambda\nu}$, respectively; and ω_λ and ω'_λ are the harmonic frequencies of a parent and substituted species, respectively.

The parameters $\mathcal{K}^e_{\alpha\beta}$ can be found from the normalization conditions

$$\sum_{\alpha} \mathcal{K}^e_{\alpha\beta}\mathcal{K}^e_{\alpha\gamma} = \sum_{\alpha} \mathcal{K}^e_{\beta\alpha}\mathcal{K}^e_{\gamma\alpha} = \delta_{\beta\gamma} \quad [4]$$

and

$$\sum_{\beta} J^e_{\alpha\beta}\mathcal{K}^e_{\beta\gamma} = I'^e_{\gamma\gamma}\mathcal{K}^e_{\alpha\gamma}, \quad [5]$$

where $I'^e_{\gamma\gamma}$ denotes the equilibrium moments of inertia of the substituted molecule. The terms $J^e_{\alpha\beta}$ are determined by the formulae

$$J^e_{\alpha\beta} = \sum_{\gamma\delta\kappa} \varepsilon_{\alpha\gamma\kappa}\varepsilon_{\beta\delta\kappa} j^e_{\gamma\delta} \quad [6]$$

and

$$j^e_{\gamma\delta} = j^e_{\delta\gamma} = \sum_N m'_N r^e_{N\gamma} r^e_{N\delta} - \frac{\sum_K m'_K r^e_{K\gamma} \sum_L m'_L r^e_{L\delta}}{\sum_N m'_N}. \quad [7]$$

Here $r^e_{N\alpha}$ are the Cartesian coordinates defining the equilibrium positions of the nuclei of the "mother" species in the molecule-fixed axis system. The values $\mathcal{K}^e_{\alpha\gamma}$ can be also considered as the eigenvectors of the "inertia tensor" $J^e_{\alpha\beta}$ with the eigenvalues $I'^e_{\gamma\gamma}$.

Further use of Eq. [1] in customary formulae of conventional vibration–rotation theory (see, e.g., (*13, 14*)) allows one, in principle, to establish connections with other spectroscopic parameters of different isotopic species. It should be mentioned, however, that Eq. [1], in the general case, is very complicated, and the values occurring in the right-hand side of Eq. [1] may be determinable only numerically and in consequence, isotopic relations may also be obtained only numerically. The main reason for this limitation is the complicated form of the transformation coefficients $l_{N\alpha\mu}$ of the "mother" species.

As was shown (*15*), the transformation coefficients $l_{N\alpha\mu}$ of the "mother" species have a very simple form, which for convenience is reproduced again in Table 1, when an XH_3 molecule (with C_{3v} symmetry) possesses some special properties, namely

(a) the ratio of the atomic masses m_H/m_X is small;
(b) the equilibrium angles H–X–H are close to $\pi/2$;
(c) there are no interactions between stretching and bending motions in the quadratic part of intramolecular potential function, i.e., parameters f_{rr}, $f_{rr'}$, $f_{\alpha\alpha}$, and $f_{\alpha\beta}$ are nonzero, but $f_{r\alpha} = f_{r\beta} = 0$.

In case these approximations are valid one can expect that analogous simple relations can also be derived for a "daughter"

TABLE 1
Values of $l_{N\alpha\lambda_s}$ Parameters of an XY_3 Molecule in the Local Mode Limit[a]

N	α	λ	s	$l_{N\alpha\lambda}$	N	α	λ	s	$l_{N\alpha\lambda}$
1	x	1		$\sqrt{2}/3$	1	x	2		$1/3$
2	x	1		$-\sqrt{2}/6$	2	x	2		$-1/6$
3	x	1		$-\sqrt{2}/6$	3	x	2		$-1/6$
1	y	1		0	1	y	2		0
2	y	1		$-1/\sqrt{6}$	2	y	2		$-1/2\sqrt{3}$
3	y	1		$1/\sqrt{6}$	3	y	2		$1/2\sqrt{3}$
1	z	1		$-1/3$	1	z	2		$\sqrt{2}/3$
2	z	1		$-1/3$	2	z	2		$\sqrt{2}/3$
3	z	1		$-1/3$	3	z	2		$\sqrt{2}/3$
1	x	3	1	$2/3$	1	x	4	1	$1/3\sqrt{2}$
2	x	3	1	$1/6$	2	x	4	1	$-\sqrt{2}/3$
3	x	3	1	$1/6$	3	x	4	1	$-\sqrt{2}/3$
1	y	3	1	0	1	y	4	1	0
2	y	3	1	$1/2\sqrt{3}$	2	y	4	1	$1/\sqrt{6}$
3	y	3	1	$-1/2\sqrt{3}$	3	y	4	1	$-1/\sqrt{6}$
1	z	3	1	$-\sqrt{2}/3$	1	z	4	1	$1/3$
2	z	3	1	$1/3\sqrt{2}$	2	z	4	1	$-1/6$
3	z	3	1	$1/3\sqrt{2}$	3	z	4	1	$-1/6$
1	x	3	2	0	1	x	4	2	0
2	x	3	2	$1/2\sqrt{3}$	2	x	4	2	$1/\sqrt{6}$
3	x	3	2	$-1/2\sqrt{3}$	3	x	4	2	$-1/\sqrt{6}$
1	y	3	2	0	1	y	4	2	$-1/\sqrt{2}$
2	y	3	2	$1/2$	2	y	4	2	0
3	y	3	2	$1/2$	3	y	4	2	0
1	z	3	2	0	1	z	4	2	0
2	z	3	2	$1/\sqrt{6}$	2	z	4	2	$-1/2\sqrt{3}$
3	z	3	2	$-1/\sqrt{6}$	3	z	4	2	$1/2\sqrt{3}$

[a] All parameters $l_{4\alpha\lambda_s}$ are equal to zero.

species on the basis of the general expression [1]. Here we consider the case in which only one H atom is substituted by a D atom (atom 1 in Fig. 1). In this case, making use of the conditions (a)–(c) as defined above in the general formulae [2]–[7] yields the following simple nonzero values of the $\mathcal{K}^e_{\alpha\beta}$ and $\beta_{\lambda\mu}$ coefficients:

$$\mathcal{K}^e_{xx} = 1/\sqrt{3} \quad \mathcal{K}^e_{xz} = -\sqrt{2/3} \quad \mathcal{K}^e_{zx} = \sqrt{2/3}$$
$$\mathcal{K}^e_{zz} = 1/\sqrt{3} \quad \mathcal{K}^e_{yy} = 1; \qquad [8]$$

$$\beta_{11} = \sqrt{2/3} \quad \beta_{21} = \sqrt{2/3} \quad \beta_{13_1} = -1/\sqrt{3} \quad \beta_{23_1} = 2/\sqrt{3}$$
$$\beta_{32} = 1/\sqrt{3} \quad \beta_{42} = 2\sqrt{2}/3 \beta_{34_1} = -\sqrt{2/3} \quad \beta_{44_1} = 2/3$$
$$\beta_{53_2} = 1 \quad \beta_{64_2} = 2/\sqrt{3}. \qquad [9]$$

From the above discussion it is clear that the $\mathcal{K}^e_{\alpha\gamma}$ coefficients can be also considered as the elements of the matrix which describe a rotation of the molecular fixed coordinate axis under isotopic substitution $XH_3 \rightarrow XH_2D$. In this case, it may be interesting to discuss the accuracy of the used local mode approximation. This can be made, for example, by comparing the value of the angle χ under rotation of the intramolecular coordinate axis both in the local mode model, and in the "realistic" case (i.e., $m_H/M \neq 0$; $\alpha_e \neq 90^\circ$). In this present case, as can seen from the above discussion, the rotation is performed about the y axis. Figure 2 shows the dependence of the value of the angle χ on the values of the mass M ($m_H = 1$) and the equilibrium interbond angle α_e. Here, point A corresponds to the local mode model (m_H/M close to zero; $\alpha_e = 90^\circ$); point B corresponds the actual PH_3 molecule ($m_H/M_P = 1/31$; $\alpha_e = 93.45^\circ$ (*16*)). As the calculations show, the differences in the $\mathcal{K}^e_{\alpha\gamma}$ values between the local mode model and the "realistic" one may achieve values of 20–25% for the substitution $PH_3 \rightarrow PH_2D$. At the same time, Fig. 2 shows that the values of such differences are decreasing rapidly with increasing mass M and/or decreasing value of ($\alpha_e - 90^\circ$). For example, for the $AsH_3 \rightarrow AsH_2D$ substitution, the above mentioned differences in the $\mathcal{K}^e_{\alpha\gamma}$ values are as small as 4–6%.

Using relations [8], [9] and the values of the transformation coefficients $l_{N\alpha\mu}$ of the "mother" molecule XH_3 as reported in Table 1 in the general formula [1], one can obtain without difficulties very simple relations for the $l'_{K\beta\lambda}$ transformation

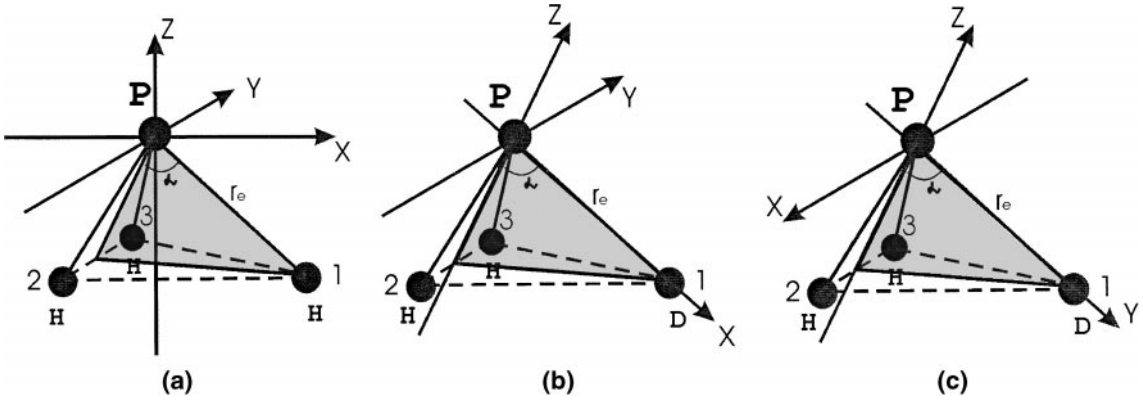

FIG. 1. (a) Orientation of the coordinate axis in the "mother" XH_3 molecule. (b) Orientation of the coordinate axis in the "daughter" XH_2D molecule after rotation. (c) Orientation of the coordinate axis which corresponds to the III^I representation in the XH_2D molecule.

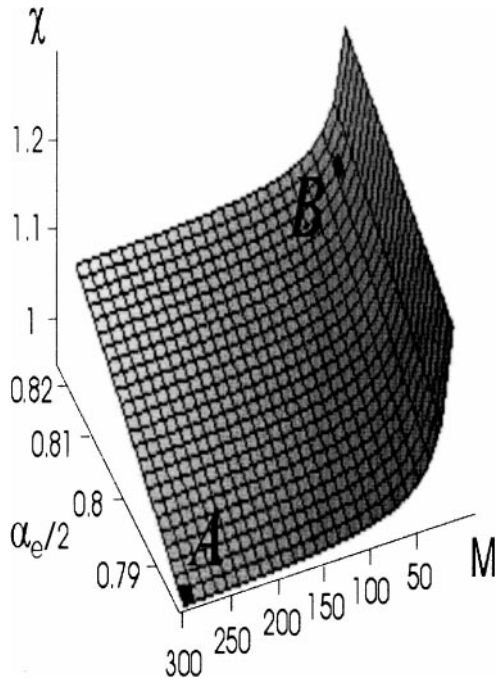

FIG. 2. The dependence of the value of the angle χ (in radians) on the value of the mass M (in u) of the X nucleus and the value of the equilibrium interbond angle α_e (in radians) is shown. Here the angle χ is the angle of rotation of the molecular fixed coordinate axis under $XH_3 \rightarrow XH_2D$ substitution. Point A corresponds to the local mode model (m_H/M close to zero; $\alpha_e = 90^\circ$); point B corresponds the PH_3 molecule ($m_H/M_P = 1/31$; $\alpha_e = 93.45^\circ$ (*13*)).

coefficients for the XH_2D species. It should be mentioned that the relations Eq. [8] determine the rotation of the molecular coordinate axis from the configuration shown in Fig. 1a to the configuration illustrated in Fig. 1b. At the same time, as was discussed in (*11*), the coordinate axes for the PH_2D molecule should be oriented as shown in Fig. 1c. This means that the indices β appearing in the transformation coefficients $l'_{K\beta\lambda}$ determined as described above should be relabelled in accordance with the axis in Fig. 1c. The coefficients $l'_{K\alpha\lambda}$ eventually obtained are presented in Table 2.

These coefficients are the basis to derive simple expressions for different rovibrational parameters, such as Coriolis coefficients $\zeta'^{\alpha}_{\lambda\mu}$ and rotation–vibration coefficients $a'^{\alpha\beta}_{\lambda}$. These Coriolis coefficients $\zeta'^{\alpha}_{\lambda\mu}$ and ro-vibrational parameters $a^{\alpha\beta}_{\lambda}$, respectively, are given in

$$\zeta'^{x}_{1,4} = -\zeta'^{x}_{2,4} = -\zeta'^{x}_{3,4} = \zeta'^{x}_{5,6} = -\zeta'^{z}_{1,6} = \zeta'^{z}_{2,6} = -\zeta'^{z}_{3,6} = \zeta'^{z}_{4,5} = -1/\sqrt{3}, \quad \zeta'^{y}_{3,5} = -1, \quad \zeta'^{y}_{4,6} = 1/3; \qquad [10]$$

$$a^{xx}_1 = a^{yy}_1/2 = a^{zz}_1 = a^{xx}_2/2 = a^{zz}_2/2 = -a^{xx}_3 = a^{zz}_3 = -a^{xz}_5 = -a^{zx}_5 = \sqrt{2m_H r_e^2},$$

$$a^{yz}_4 = a^{zy}_4 = a^{xy}_6 = a^{yx}_6 = -2\sqrt{2m_H r_e^2}/\sqrt{3}. \qquad [11]$$

In turn, we have used Eqs. [10] and [11] to calculate rotational–vibrational spectroscopic parameters $\alpha'^{\beta}_{\lambda}$ of PH_2D. In this case, the same above-mentioned approximation for the intramolecular potential function as for the "mother" molecule PH_3 (*15*) was used, too, for PH_2D. We have derived simple isotopic relations for the rotation–vibration parameters of the bending modes:

$$\begin{aligned}
\alpha'^{x}_3 &= \alpha'^{z}_3 = \frac{8}{9}\frac{B_e^2}{\theta\omega}(\theta^2 - 1 + 2c);\\
\alpha'^{x}_4 &= \alpha'^{z}_6 = \frac{4}{27\sqrt{3}}\frac{B_e^2}{\theta\omega}(42\theta^2 - 23 + 9c/2)\\
&\quad + \frac{16}{27\sqrt{3}}\frac{B_e^2}{\theta\omega}\left(\frac{4+9\theta^2}{4-3\theta^2} + \frac{2+9\theta^2}{2-3\theta^2}\right);\\
\alpha'^{x}_6 &= \alpha'^{z}_4 = \frac{28}{9\sqrt{3}}\frac{B_e^2}{\theta\omega}(2\theta^2 - 1 + 3c/14)\\
&\quad + \frac{16}{27\sqrt{3}}\frac{B_e^2}{\theta\omega}\left(\frac{4+9\theta^2}{4-3\theta^2}\right);\\
\alpha'^{y}_3 &= 4\frac{B_e^2}{\theta\omega}\left(\frac{3-\theta^2}{1-\theta^2}\right)\theta^2;\\
\alpha'^{y}_4 &= \alpha'^{y}_6 = \frac{4}{3\sqrt{3}}\frac{B_e^2}{\theta\omega}(3\theta^2 - 4 + 9c/4);
\end{aligned} \qquad [12]$$

Column 2 of Table 3 reports the calculated values for the bending vibrations ν_3, ν_4, and ν_6. The Coriolis interaction parameters $A\zeta$, $B\zeta$, and $C\zeta$ were calculated using the relations of Eq. [10] and the rotational constants A, B, and C from Ref. (*11*). The B_e value was taken as $B_e = h/(8\pi^2 c)(2m_H r_e^2)^{-1} = 4.2276\ \text{cm}^{-1}$, with $r_e = 1.412$ Å taken from Ref. (*17*); the frequency ω is $(\omega_1 + \omega_3)/2 = 2324\ \text{cm}^{-1}$. The empirical parameter $\theta = (\theta_1 + \theta_2)/2 = 0.444\ \text{cm}^{-1}$ was estimated from the three quartic centrifugal

TABLE 2
Values of Nonzero $l_{N\alpha\lambda}$ Parameters of an XH_2D Molecule in the Local Model Limit[a]

N	α	λ	$l_{N\alpha\lambda}$	N	α	λ	$l_{N\alpha\lambda}$
2	x	1	1/2	2	y	4	$-1/\sqrt{3}$
3	x	1	$-1/2$	3	y	4	$-1/\sqrt{3}$
2	z	1	$-1/2$	1	z	4	$1/\sqrt{3}$
3	z	1	$-1/2$	2	x	5	$-1/2$
1	y	2	1	3	x	5	$-1/2$
2	x	3	1/2	2	z	5	1/2
3	x	3	$-1/2$	3	z	5	$-1/2$
2	z	3	1/2	1	x	6	$1/\sqrt{3}$
3	z	3	1/2	2	y	6	$1/\sqrt{3}$
				3	y	6	$-1/\sqrt{3}$

[a] All parameters $l_{4\alpha\lambda}$ are equal to zero.

TABLE 3
Some Coriolis Interactions and Vibration–Rotation Parameters of the PH_2D Molecule (in cm^{-1})

Parameter	Value[a)]	Value[b)]
1	2	3
$B\zeta^x_{43}$	-1.72	-2.07
$C\zeta^x_{46}$	1.45	1.59
$A\zeta^x_{36}$	1.60	1.52
α^x_3	-0.0006	-0.0011
α^y_3	0.0477	0.0479
α^z_3	-0.0006	0.0051
α^x_4	0.0066	0.0044
α^y_4	-0.0340	-0.0317
α^z_4	-0.0063	-0.0076
α^x_6	-0.0063	-0.0089
α^y_6	-0.0340	-0.0450
α^z_6	0.0066	0.0113

[a] Predicted on the basis of derived isotopic relations.
[b] Obtained from the fit of experimental data.

distortion coefficients of the PH_3 molecule in the ground vibrational state, Ref. (*8*), with the formulae

$$D_J = \frac{B_e^3}{3\omega^2}\left(9+\theta_2^{-2}+2\theta_4^{-2}\right),\quad D_{JK} = \frac{2B_e^3}{\omega^2}\left(1-\theta_2^{-2}\right),$$
$$D_K = \frac{B_e^3}{3\omega^2}\left(-7+9\theta_2^{-2}-2\theta_4^{-2}\right), \qquad [13]$$

taken from Ref. (*15*). Parameter c in Eq. [12] can be determined, on the one hand, from an experimental value of one of the α^β_λ rotation–vibration constants of the "mother" molecule PH_3 or, on the other hand, can be taken as an empirical parameter of the PH_2D molecule. In the present analysis it was set to 0.38.[1]

The parameters given in column 2 of Table 3 were used as the starting values for fitting the experimental rovibrational energies of the (001000), (000100), and (000001) vibrational states of the PH_2D molecule.

3. EXPERIMENTAL SECTION

The synthesis of phosphine enriched to 60% PHD_2, 25% PH_2D, 10% PD_3, and 5% PH_3 (sample A) has been described (*11*). Moreover, a sample composed of 5% PH_2D, 10% PHD_2, and 85% PD_3 (sample B) was available for comparison and identification of lines belonging to other isotopomers than PH_2D by means of relative intensities of lines.

Spectra were recorded at room temperature with a Bruker 120 HR interferometer adjusted to a resolution of 2.3×10^{-3} cm^{-1} (1/maximum optical path difference) in the region 600–1160 cm^{-1}. A Globar source, a KBr/Ge beam splitter, and an MCT 600 detector were employed, and a 8.5 μm low-pass filter was inserted. A 28-cm glass cell fitted with KBr windows was used, with pressures ranging from 100 to 550 Pa. Between 150 and 400 scans were collected for the different spectra. Calibration was done with CO_2 lines (*18*); wavenumber precision of unblended, medium intensity lines is about 1×10^{-4} cm^{-1}. It was ensured that wavenumbers of different spectra were compatible with each other within one precision interval. Two portions of the spectrum are illustrated in Figs. 3 and 4, and some assignments are given.

4. HAMILTONIAN MODEL AND WAVE FUNCTIONS

4.1. Rovibrational Hamiltonian

As was discussed in (*11*), the PH_2D molecule is an asymmetric top very close to the prolate symmetric top limit, and III^l representation of the rotational Watson-type Hamiltonian in A reduction is very efficient. This is taken as

$$\begin{aligned}H^{ii} = {} & E^i + \left[A^i - \frac{1}{2}(B^i+C^i)\right]J_z^2 + \frac{1}{2}(B^i+C^i)J^2 \\ & + \frac{1}{2}(B^i-C^i)J_{xy}^2 - \Delta_K^i J_z^4 - \Delta_{JK}^i J_z^2 J^2 \\ & - \Delta_J^i J^4 - \delta_K^i\left[J_z^2, J_{xy}^2\right] - 2\delta_J^i J^2 J_{xy}^2 + H_K^i J_z^6 \\ & + H_{KJ}^i J_z^4 J^2 + H_{JK}^i J_z^2 J^4 + H_J^i J^6 + \left[J_{xy}^2, h_K^i J_z^4\right. \\ & \left. + h_{JK}^i J^2 J_z^2 + h_J^i J^4\right] + L_K^i J_z^8 + L_{KKJ}^i J_z^6 J^2 \\ & + L_{JK}^i J_z^4 J^4 + L_{KJJ}^i J_z^2 J^6 + L_J^i J^8 + \left[J_{xy}^2, l_K^i J_z^6\right. \\ & \left. + l_{KJ}^i J^2 J_z^4 + l_{JK}^i J^4 J_z^2 + l_J^i J^6\right] + \cdots, \end{aligned} \qquad [14]$$

where the condition $B_y > B_x > B_z$ is fulfilled, $J_{xy}^2 = J_x^2 - J_y^2$, and $J^2 = J_x^2 + J_y^2 + J_z^2$. The PH_2D molecule has C_s symmetry. Its three lowest vibrational bands, ν_4, ν_6, and ν_3, have A′, A″, and A′ symmetries, respectively, and interact strongly with each other. On this reason, a Hamiltonian was used which has the form

$$H^{v.-r.} = \sum_{i,j} |i\rangle\langle j| H^{ij}, \qquad [15]$$

where $i = 4$, 3, 6, and $|4\rangle = (000100)$, $|3\rangle = (001000)$, and $|6\rangle = (000001)$. The diagonal parts H^{ii} have the form of Eq. [14]. Interactions between the states (000100) and (001000) on the one hand and the state (000001) on the other hand are described by the H^{i6} ($i = 3$ or 4) operators

$$H^{i6} = H^{6i^+} = H_{C_z}^{i6} + H_{C_y}^{i6}, \qquad [16]$$

[1] In the first step of the analysis, values of the rotational parameters were roughly estimated from the fit of the energy levels with the quantum number $J = 0$ and 1. The α^β_λ parameters obtained from just that fit were used to estimate the coefficient of the c value.

where

$$H^{i6}_{C_z} = 2(A\zeta^z)^{i6} i J_z + C^{i6}_{zK} i J_z^3 + + C^{i6}_{zJ} i J_z J^2 + C^{i6}_{zKK} i J_z^5 + C^{i6}_{zJK} i J_z^3 J^2 + C^{i6}_{zJJ} i J_z J^4 + C^{i6}_{zKKK} i J_z^7 + \cdots + C^{i6}_{xy}[J_x, J_y]_+ C^{i6}_{xyK}\left[[J_x, J_y]_+, J_z^2\right]_+ + C^{i6}_{xyJ}[J_x, J_y]_+ J^2 + C^{i6}_{xyKK}\left[[J_x, J_y]_+, J_z^4\right]_+ + C^{i6}_{xyJK}\left[[J_x, J_y]_+, J_z^2 J^2\right]_+ + C^{i6}_{xyJJ}[J_x, J_y]_+ J^4 + \cdots \quad [17]$$

and

$$H^{i6}_{C_y} = 2(B\zeta^y)^{i6} i J_y + C^{i6}_{yK}\left[i J_y, J_z^2\right]_+ + C^{i6}_{yJ} i J_y J^2 + C^{i6}_{yKK}\left[i J_y, J_z^4\right]_+ + C^{i6}_{yJK}\left[i J_y, J_z^2 J^2\right]_+ + C^{i6}_{yJJ} i J_y J^4 + C^{i6}_{yKKK}\left[i J_y, J_z^6\right]_+ + C^{i6}_{yKKJ}\left[i J_y, J_z^4 J^2\right]_+ \cdots + C^{i6}_{xz}[J_x, J_z]_+ + C^{i6}_{xzK}\left[[J_x, J_z]_+, J_z^2\right]_+ + C0^{i6}_{xzJ}[J_x, J_z]_+ J^2 + C^{i6}_{xzKK}\left[[J_x, J_z]_+, J_z^4\right]_+ + C^{i6}_{xzJK}\left[[J_x, J_z]_+, J_z^2 J^2\right]_+ + C^{i6}_{xzJJ}[J_x, J_z]_+ J^4 + \cdots. \quad [18]$$

In turn, the resonance interaction operator $H^{43} = H^{34+}$ has the form

$$H^{43} = H^{43}_F + H^{43}_{C_x}, \quad [19]$$

where

$$H^{43}_F = F^{43} + F^{43}_K J_z^2 + F^{43}_J J^2 + F^{43}_{KK} J_z^4 + F^{43}_{JK} J_z^2 J^2 + F^{43}_{JJ} J^4 + F^{43}_{KKK} J_z^6 + F^{43}_{KJJ} J_z^2 J^4 + \cdots + F^{43}_{xy} J_{xy}^2 + F^{43}_{xyK}\left[J_{xy}^2, J_z^2\right]_+ + F^{43}_{xyJ} J_{xy}^2 J^2 + F^{43}_{xyKK}\left[J_{xy}^2, J_z^4\right]_+ + F^{43}_{xyJK}\left[J_{xy}^2, J_z^2 J^2\right]_+ + \cdots. \quad [20]$$

and

$$H^{43}_{C_x} = 2(B\zeta^x)^{43} i J_x + C^{43}_{xK}\left[i J_x, J_z^2\right]_+ + C^{43}_{xJ} i J_x J^2 + \cdots + C^{43}_{yz}[J_y, J_z]_+ + C^{43}_{yzK}\left[[J_y, J_z]_+, J_z^2\right]_+ + C^{43}_{yzJ}[J_y, J_z]_+ J^2 + C^{43}_{yzKK}\left[[J_y, J_z]_+, J_z^4\right]_+ + \cdots. \quad [21]$$

4.2. Rotational Wave Functions

In order to make the Hamiltonian matrix real, we have defined the wave functions as follows.

1. Symmetric rotational wave functions:

$$|JK, A'\rangle = \frac{i^J}{\sqrt{2}}\{|JK\rangle + (-1)^J |J - K\rangle\}$$

for $K = 2, 4, 6, \ldots$;

$$|JK, A'\rangle = \frac{i^{J+1}}{\sqrt{2}}\{|JK\rangle + (-1)^J |J - K\rangle\}$$

for $K = 1, 3, 5, \ldots$;

$$|J0, A'\rangle = i^J |J0\rangle$$

for J even.

2. Antisymmetric rotational wave functions:

$$|JK, A''\rangle = \frac{i^{J-1}}{\sqrt{2}}\{|JK\rangle - (-1)^J |J - K\rangle\}$$

for $K = 2, 4, 6, \ldots$;

$$|JK, A''\rangle = \frac{i^J}{\sqrt{2}}\{|JK\rangle - (-1)^J |J - K\rangle\}$$

for $K = 1, 3, 5, \ldots$;

$$|J0, A''\rangle = i(J - 1)|J0\rangle$$

for J odd.

These functions were employed to set up the Hamiltonian matrix which was then used to fit the experimental data.

5. ASSIGNMENT AND RESULTS

While the ν_3 and ν_4 bands should be associated both with *a*- and *c*-type transitions, the ν_6 band is expected to reveal *b*-type structure. Indeed, all three types of transitions were observed in the bending triad band. In this case, the comparison of the "pilot" transitions, $(J'K'_a = J'K'_c) \leftarrow (JK_a = JK_c)$, $(K'_c, K_c = 0$ and/or 1), for all three bands shows that the strengths of the *a*- and *c*-type transitions are not much different from each other in the ν_3 band. The same can be seen in the ν_4 band. At the same time, transitions of the ν_3 band are slightly weaker (about 15–20%) than corresponding transitions of the ν_4 band. As to the ν_6 band, the strengths of its "pilot" transitions are comparable with those of the corresponding "pilot" transitions of the ν_4 band.

Assignments were made using the ground state combination differences method, with ground state rotational energies taken from Ref. (*11*). For convenience, the ground state rotational parameters are included in Table 4 and given in column 2. The

TABLE 4
Rotational and Centrifugal Distortion Parameters for the Ground and the Bending Vibrational States of PH_2D (in cm^{-1})[a]

Parameter	(000000)	(001000)	(000100)	(000001)
1	2	3	4	5
ν		1092.5573590(616)	892.9275476(600)	969.4810870(612)
A	2.78247196	2.7773997(996)	2.7900553(973)	2.7710934E(492)
B	2.98320620	2.9842695(550)	2.9787664(559)	2.99206545(621)
C	4.33657995	4.2886767(452)	4.3683207(459)	4.38163113(666)
$\Delta_K \times 10^4$	-0.873198	-0.88840(874)	-0.86470(920)	-0.88542(125)
$\Delta_{JK} \times 10^4$	0.639662	0.65733(754)	0.62208(198)	0.638184(456)
$\Delta_J \times 10^4$	0.600698	0.60487(116)	0.625370(112)	0.627852(348)
$\delta_K \times 10^4$	-0.777525	-0.777525	-0.777525	-0.777525
$\delta_J \times 10^4$	-0.075385	-0.075385	-0.075385	-0.075385
$H_K \times 10^8$	-0.90645	-0.90645	-0.90645	-0.90645
$H_{KJ} \times 10^8$	0.3123	0.3123	0.3123	0.3123
$H_{JK} \times 10^8$	0.3896	0.3896	0.3896	0.3896
$H_J \times 10^8$	0.30497	0.30497	0.30497	0.30497
$h_K \times 10^8$	0.25038	0.25038	0.25038	0.25038
$h_{JK} \times 10^8$	-0.92844	-0.92844	-0.92844	-0.92844
$h_J \times 10^8$	-0.08227	-0.08227	-0.08227	-0.08227
$L_K \times 10^{12}$	-6.524	-6.524	-6.524	-6.524
$L_{KKJ} \times 10^{12}$	14.354	14.354	14.354	14.354
$L_{JK} \times 10^{12}$	-9.298	-9.298	-9.298	-9.298
$L_{KJJ} \times 10^{12}$	1.9422	1.9422	1.9422	1.9422
$L_J \times 10^{12}$	-0.4997	-0.4997	-0.4997	-0.4997
$l_K \times 10^{12}$	-1.951	-1.951	-1.951	-1.951
$l_{KJ} \times 10^{12}$	1.702	1.702	1.702	1.702
$l_{JK} \times 10^{12}$	0.0	0.0	0.0	0.0
$l_J \times 10^{12}$	0.2114	0.2114	0.2114	0.2114

Note. Excited state parameters without confidence intervals given were fixed to the values of corresponding parameters of the ground vibrational state.

[a] Values in parentheses are 1σ statistical confidence intervals.

present body of assignments comprised

$$\nu_4,\ J^{max} = 22, \quad K_c^{max} = 17, \quad n = 2560$$
$$\nu_3,\ J^{max} = 21, \quad K_c^{max} = 15, \quad n = 1590$$
$$\nu_6,\ J^{max} = 20, \quad K_c^{max} = 14, \quad n = 1350.$$

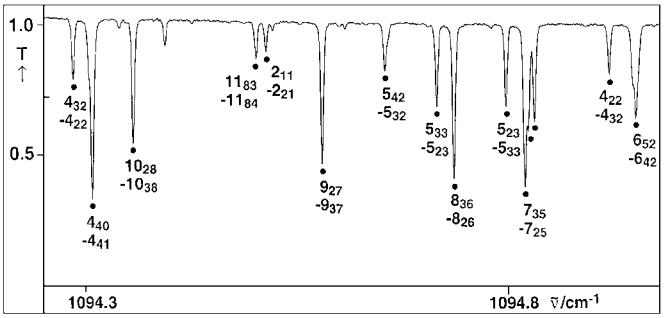

FIG. 3. Part of the PH_2D spectrum in the region of the Q-branch of the ν_3 band. Lines of PH_2D are denoted by a dot, and their $J'_{K'_a K'_c} - J''_{K''_a K''_c}$ assignment is given. Unassigned lines belong to other isotopic species (PHD_2, PD_3, PH_3).

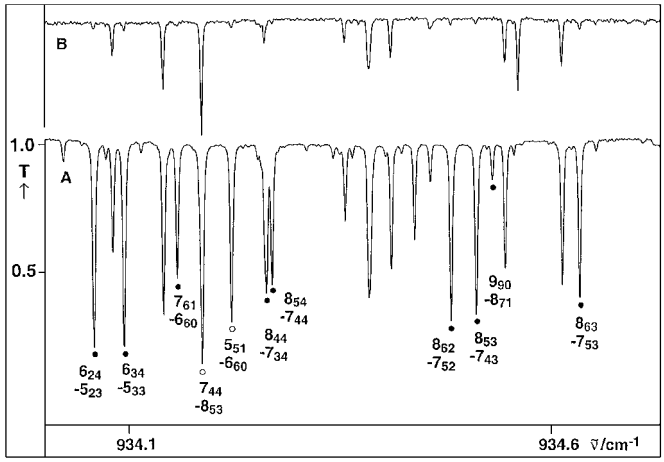

FIG. 4. Trace A: Spectrum of a mixture of PHD_2 and PH_2D. Lines belonging to PH_2D are assigned by full dots for the R branch of the ν_4 band and by open circles for the P branch of the ν_6 band. Unassigned lines belong to other isotopic species (PHD_2, PD_3, PH_3). Trace B: Spectrum of a sample richer in PD_3 and poorer in PH_2D and PH_3 shown for comparison.

TABLE 5
Some Assigned Transitions in the Q-Branch of the ν_4 Band of the PH_2D Molecule

J'	K'_a	K'_c	J	K_a	K_c	Line position[a] (cm^{-1})	Transm. (%)	ν_{exp}-ν_{calc} $10^4 cm^{-1}$	Line position[b] (cm^{-1})	ν_{exp}-ν_{calc} $10^4 cm^{-1}$
16	16	0	16	16	1	890.06237	68.5	1.5	890.0636	5.0
16	16	1	16	16	0	890.06759	69.6	0.2	890.0636	-48.0
5	3	3	5	2	3	890.16820	70.9	0.8	890.1698	8.0
15	15	0	15	15	1	890.18156	58.1	-0.7	890.1821	5.0
15	15	1	15	15	0	890.19100	54.5	-2.8	890.1907	-5.0
5	2	3	5	3	3	890.21240	73.1	0.9	890.2124	-7.0
4	1	4	4	0	4	890.27434	20.6	-0.3	890.2738	-13.0
14	14	0	14	14	1	890.29011	48.6	-2.0	890.2903	4.0
14	14	1	14	14	0	890.30714	47.8	-2.8	890.3074	4.0
17	4	13	16	1	15	890.37613	95.6	16.2		
13	13	0	13	13	1	890.38959	37.3	-2.5	890.3896	2.0
13	13	1	13	13	0	890.41938	37.3	-2.9	890.4192	0.0
3	3	1	3	2	1	890.44127	96.0	0.3		
12	12	0	12	12	1	890.48061	22.2	-2.0	890.4822	17.0
1	1	0	1	1	1	890.48350	47.5	1.2	890.4822	-1.0
15	11	5	15	11	4	890.48874	87.7	-3.5		
2	2	0	2	2	1	890.52282	30.9	-1.8	890.5237	0.0
12	12	1	12	12	0	890.53173	27.7	-2.4	890.5326	10.0
11	11	0	11	11	1	890.56247	20.3	-1.4	890.5628	3.0
3	3	0	3	3	1	890.57624	20.3	-1.0	890.5759	2.0
4	2	3	4	1	3	890.60884	62.1	-0.2	890.6102	5.0
7	5	2	7	6	2	890.61331	89.4	-1.6		
4	3	1	4	2	3	890.61999	61.3	0.0	890.6205	-2.0
4	4	0	4	4	1	890.63420	3.9	-9.0	890.6335	-11.0
11	11	1	11	11	0	890.64870	20.1	-1.4	890.6489	2.0
8	6	2	8	7	2	890.65597	91.2	-4.2		
6	4	2	6	5	2	890.68190	80.2	-1.7		
9	9	0	9	9	1	890.68888	1.5	-3.1	890.6879	-15.0
8	8	0	8	8	1	890.72577	1.3	-0.9	890.7251	-10.0
7	7	0	7	7	1	890.73889	8.7	1.7	890.7386	-3.0
8	7	2	8	7	1	890.77297	15.6	-1.0	890.7753	18.0
10	10	1	10	10	0	890.77591	12.9	0.4	890.7753	-6.0
10	8	3	10	8	2	890.79816	51.8	-0.5	890.7964	18.0
9	7	2	9	8	2	890.82761	94.9	-4.0		
5	3	2	5	4	2	890.83637	85.3	-0.2	890.8370	3.0
9	9	1	9	9	0	890.92029	10.7	1.2	890.9202	-2.0
3	1	3	3	0	3	890.94553	31.7	6.9	890.9456	0.0
3	0	3	3	1	3	890.94553	31.7	-9.3	890.9456	-15.0
4	2	2	4	3	2	891.04282	80.4	0.1	891.0427	-3.0
8	8	1	8	8	0	891.09107	8.4	2.0	891.0908	-4.0
3	2	2	3	1	2	891.12454	75.0	-0.9	891.1245	-3.0
10	8	2	10	9	2	891.13618	97.3	-1.0		
2	2	1	2	1	1	891.14401	91.4	-0.6	891.1440	4.0

[a] This work.
[b] Ref. (*10*).

In accordance with the III^l representation of the rotational Hamiltonian, rotational energies for given J increase with K_c.

The superiority of the present study to that of Ref.(*10*) can be underlined by some statistical data. Our J^{max} values, 22, 21, and 20, exceed those of (*10*), which were 20, 20, and 18, respectively, for ν_4, ν_3, and ν_6. The number of ν_4 and ν_6 band transitions, 2560 and 1350, respectively, is substantially larger than that in (*10*), 1579 and 1116. The 1590 transitions assigned for the ν_3 band seem to be less than the 1739 transitions assigned $\leq$1235 cm^{-1} in (*10*). However, our spectrum was only exploited up to 1160 cm^{-1} and the 1739 transitions should be compared with the 1357 assignments $\leq$1160 cm^{-1} in Ref. (*10*).

Thanks to the significantly improved ground state energies, the higher precision of the present data, and the greater sensitivity of the actual spectrum, averaged experimental upper state energies were determined with an accuracy of 0.23×10^{-3} cm^{-1}, which may be compared with the RMS of Ref. (*10*), ca. 0.43×10^{-3} cm^{-1}. Two details of the spectra, with assignments of PH_2D lines, are illustrated in Figs. 3 and 4. Table 5 reproducing a small part of the studied spectrum in the region of the ν_4 band center illustrates, on the one hand, that some weak lines not found in (*10*) were assigned in our study and, on the other hand, that line positions are reproduced 3–4 times more accurately. Averaged upper state energies obtained from different transitions reaching the same state are reported in Table 6, columns 2 (ν_4),

TABLE 6

Experimental Rovibrational Term Values for the (000100), (001000), and (000001) Vibrational States of the PH_2D Molecule (in cm^{-1})[a]

			(000100)			(001000)			(000001)						(000100)			(001000)			(000001)		
J	K_a	K_c	E	Δ	δ	E	Δ	δ	E	Δ	δ	J	K_a	K_c	E	Δ	δ	E	Δ	δ	E	Δ	δ
	1		2	3	4	5	6	7	8	9	10		1		2	3	4	5	6	7	8	9	10
0	0	0	891.91338	5	-23	1093.57114	7	-12	969.48071		-37	8	1	8	1186.48564	17	7	1391.54347	18	-8	1279.33403	18	2
1	1	0	897.60168	-2	-27	1099.48596	6	-1	975.17088	5	-33	8	0	8	1186.48564	17	7	1391.54347	18	-8	1279.33403	18	2
1	1	1	898.93830	6	-20	1100.71625	9	1	976.68249	11	-20	9	9	0	1145.68658	22	5	1354.50063	15	-4	1218.56007	20	-1
1	0	1	899.05788	6	-25	1100.92421	3	-1	976.98088	8	-25	9	9	1	1145.85692	12	12	1354.54018	19	-9	1218.59225	21	-13
2	2	0	908.97019	10	-17	1111.28936	9	-4	986.51104	7	-22	9	8	1	1151.08434	16	-13	1362.72247	16	16	1229.59829	22	10
2	2	1	910.19411	9	-12	1112.33571	10	-13	987.76322	13	-15	9	8	2	1152.91509	15	17	1363.49254	20	13	1230.29756	20	23
2	1	1	910.55333	5	-13	1112.95994	10	0	988.65754	6	-24	9	7	2	1154.87714	20	-16	1367.94576	19	14	1236.88707	21	17
2	1	2	914.56513	7	-14	1116.65076	9	-1	993.18872	11	-14	9	7	3	1160.45157	14	10	1371.74642	11	12	1240.91284	24	14
2	0	2	914.57266	8	-14	1116.67457	5	-7	993.22867	5	-7	9	6	3	1160.71400	15	-1	1372.95047	20	4	1243.05082	18	-5
3	3	0	926.00237	8	-17	1128.93151	10	-11	1003.42555	10	-12	9	6	4	1170.14322	17	11	1381.14366	15	-1	1252.55885	16	13
3	3	1	927.07141	8	-2	1129.74616	6	-13	1004.36121	12	-14	9	5	4	1170.15498	15	4	1381.25609	18	7	1252.81899	21	-6
3	2	1	927.79044	7	-17	1130.99323	7	3	1006.14400	8	-15	9	5	5	1182.63248	31	25	1392.96344	8	-1	1266.99353	18	6
3	2	2	931.62495	21	-1	1134.38857	10	-7	1010.25024	14	-11	9	4	5	1182.63248	31	1	1392.96785	20	6	1267.00698	18	-1
3	1	2	931.66255	18	-2	1134.50599	10	0	1010.44475	8	-13	9	4	6	1198.00080	9	13	1407.50217	22	18	1284.74849	47	39
3	1	3	938.62340	5	-3	1141.07317	6	7	1018.56157	12	-2	9	3	6	1198.00080	9	13	1407.50217	22	10	1284.74849	47	2
3	0	3	938.62355	9	-16	1141.07475	10	-2	1018.56501	18	5	9	3	7	1216.26913	18	7	1424.74790	27	29	1305.84538	19	3
4	4	0	948.67478	14	0	1152.34750	11	-21	1025.82253	15	-11	9	2	7	1216.26913	18	6	1424.74790	27	29	1305.84538	19	2
4	4	1	949.56282	12	10	1152.92685	12	-25	1026.45353	14	2	9	2	8	1237.46697	14	2	1444.67218	11	31	1330.27533	4	12
4	3	1	950.76189	10	-17	1154.99716	11	-4	1029.40130	8	-13	9	1	8	1237.46697	14	3	1444.67218	11	31	1330.27533	4	12
4	3	2	954.36325	14	12	1158.01263	8	-12	1032.96678	14	-5	9	1	9	1261.62994	15	8	1467.24334	8	-19	1358.05366	35	-22
4	2	2	954.47497	14	-7	1158.35179	11	0	1033.52118	13	-7	9	0	9	1261.62994	15	8	1467.24334	8	-19	1358.05366	35	-22
4	2	3	961.37566	10	-1	1164.75857	7	-4	1041.36617	13	1	10	10	0	1201.68589	11	8	1411.82360	15	6	1273.25031	13	2
4	1	3	961.37767	13	-3	1164.77022	12	-5	1041.38931	13	-3	10	10	1	1201.79505	20	2	1411.84433	13	9	1273.26570	15	1
4	1	4	971.17207		-23	1174.05791	14	0	1052.89052		16	10	9	1	1208.05885	24	9	1421.33830	18	28	1285.85750	16	3
4	0	4	971.17234		2	1174.05791	14	-9	1052.89072		13	10	9	2	1209.50730	11	13	1421.82830	19	24	1286.27368	15	-9
5	5	0	976.95840	14	10	1181.47536	15	-26	1053.62730	7	6	10	8	2	1212.22094	11	6	1427.64272	17	5	1294.70018	17	18
5	5	1	977.65882	14	6	1181.85412	13	-32	1054.01546	16	-7	10	8	3	1217.30136	15	-2	1430.71152	10	-2	1297.77234	17	18
5	4	1	979.45673	13	-10	1184.93243	13	-2	1058.37090	22	-8	10	7	3	1217.77546	12	6	1432.68723	23	5	1301.15407	18	-1
5	4	2	982.77271	21	1	1187.50071	15	-5	1061.31145	11	-1	10	7	4	1226.98740	13	7	1440.26219	19	-3	1309.67682	19	13
5	3	2	983.02908	16	0	1188.24326	19	12	1062.50307	16	-4	10	6	4	1227.01529	10	11	1440.51362	16	-6	1310.24213	17	-15
5	3	3	989.81764	18	3	1194.36456	10	1	1069.88671	14	3	10	6	5	1239.42107	9	14	1452.03224	18	-3	1324.01937	14	1
5	2	3	989.82580	16	5	1194.41058	6	3	1069.97715	13	-2	10	5	5	1239.42170	18	3	1452.04506	12	-7	1324.05838	22	0
5	2	4	999.59722	20	-1	1203.65139	10	12	1081.37125	6	13	10	5	6	1254.73755	20	26	1466.51811	20	11	1341.63219	11	14
5	1	4	999.59722	20	-9	1203.65224	-	13	1081.37335	7	16	10	4	6	1254.73755	20	26	1466.51811	20	-20	1341.63367	3	19
5	1	5	1012.22406	16	0	1215.60695	13	-5	1096.16377		26	10	4	7	1272.95434	32	45	1483.73454	16	13	1362.59840	18	17
5	0	5	1012.22406	16	0	1215.60695	13	-6	1096.16377		25	10	3	7	1272.95434	32	-12	1483.73454	16	13	1362.59840	18	14
6	6	0	1010.82360	16	12	1216.27219	12	-19	1086.80294	17	1	10	3	8	1294.09850	12	-5	1503.64989	17	38	1386.89747	20	12
6	6	1	1011.34878	9	15	1216.50303	15	-23	1087.02554	11	10	10	2	8	1294.09850	12	3	1503.64989	17	38	1386.89747	20	12
6	5	1	1013.85964	12	-9	1220.74444	16	0	1092.97161	16	6	10	2	9	1318.20334	16	-9	1526.23435	16	37	1414.53393	19	-1
6	5	2	1016.84476	15	16	1222.82538	17	-5	1095.25244	18	3	10	1	9	1318.20334	16	-9	1526.23435	16	37	1414.53393	19	-1
6	4	2	1017.34164	17	-3	1224.18400	12	8	1097.38833	19	3	10	1	10	1345.30710	15	1	1551.44534	20	-29	1445.53990	15	-27
6	4	3	1023.94900	18	10	1229.88364	9	11	1104.11957	10	2	10	0	10	1345.30710	15	1	1551.44534	20	-29	1445.53990	15	-27
6	3	3	1023.97348	20	13	1230.01804	16	1	1104.37994	11	-11	11	11	0	1263.19339	22	-14	1474.75083	17	30	1333.33308	30	-3
6	3	4	1033.70720	16	10	1239.16037	17	8	1115.57176	4	2	11	11	1	1263.26162	18	-13	1474.76123	3	11	1333.34125	18	-9
6	2	4	1033.70761	20	11	1239.16448	10	3	1115.58189	12	-3	11	10	1	1270.58738	14	-2	1485.53236	11	16	1347.44768	12	0
6	2	5	1046.31075	17	10	1251.09767	21	21	1130.29668	22	22	11	10	2	1271.68844	14	13	1485.82940	11	17	1347.68490	29	-3
6	1	5	1046.31075	17	10	1251.09767	21	16	1130.29668	22	6	11	9	2	1275.27702	11	-38	1493.09690	10	0	1357.98802	16	10
6	1	6	1061.78815	15	1	1265.71171	19	-14	1148.35173	17	18	11	9	3	1279.80862	14	-4	1495.45618	6	-12	1360.19699	20	7
6	0	6	1061.78815	15	1	1265.71171	19	-14	1148.35173	17	18	11	8	3	1280.60329	10	-28	1498.43528	10	-11	1365.11822	12	5
7	7	0	1050.24487	9	12	1256.71548	17	-24	1125.34471	16	0	11	8	4	1289.51052	11	2	1505.24979	18	-5	1372.49822	21	6
7	7	1	1050.62042	12	20	1256.84868	9	-30	1125.46575	15	0	11	7	4	1289.57045	12	-4	1505.75694	9	-22	1373.59671	10	-8
7	6	1	1053.95037	15	-8	1262.36400	18	3	1133.10418	19	14	11	7	5	1301.88027	9	11	1516.97996	10	-21	1386.78484	29	15
7	6	2	1056.56806	16	16	1263.95536	16	-3	1134.75440	16	14	11	6	5	1301.88233	2	14	1517.01368	8	-21	1386.88415	8	0
7	5	2	1057.42243	16	-11	1266.14867	22	17	1138.13191	17	-13	11	6	6	1317.13485	13	13	1531.39593		-46	1404.23647	16	-1
7	5	3	1063.76777	17	-2	1271.30179	18	0	1144.05166	25	5	11	5	6	1317.13485	13	13	1531.39699		-50	1404.24113	14	-5
7	4	3	1063.82888	10	1	1271.62379	16	3	1144.66139	18	-1	11	5	7	1335.29285	17	-10	1548.56894	10	-15	1425.05141	19	7
7	4	4	1073.50182	9	10	1280.58244	19	9	1155.50093	16	8	11	4	7	1335.29285	17	25	1548.56894	10	-17	1425.05141	19	-6
7	3	4	1073.50341	12	21	1280.59750	19	8	1155.53727	22	0	11	4	8	1356.37551	16	-12	1568.46332	14	11	1449.20467	9	24
7	3	5	1086.07531	22	8	1292.49052	10	14	1170.14007	10	7	11	3	8	1356.37551	16	15	1568.46332	14	11	1449.20467	9	24
7	2	5	1086.07531	22	7	1292.49080	11	13	1170.14080	32	-12	11	3	9	1380.41526	7	-11	1591.04949	10	26	1476.68707	10	24
7	2	6	1101.52324	7	2	1307.09079	9	6	1188.11477	11	14	11	2	9	1380.41526	7	-10	1591.04949	10	26	1476.68707	10	24
7	1	6	1101.52324	7	2	1307.09079	9	6	1188.11477	11	13	11	2	10	1407.44826	20	-21	1616.29326	26	56	1507.51904	17	-5
7	1	7	1119.87314	15	7	1324.36146	20	-10	1209.42078	10	24	11	1	10	1407.44826	20	-21	1616.29326	26	56	1507.51904	17	-5
7	0	7	1119.87314	15	7	1324.36146	20	-10	1209.42078	10	24	11	1	11	1437.51510	8	-4	1644.13217	9	-23	1541.75093	20	-39
8	8	0	1095.20334	14	7	1302.79448	16	-19	1169.26067	17	1	11	0	11	1437.51510	8	-4	1644.13217	9	-23	1541.75093	20	-39
8	8	1	1095.46083	8	13	1302.86824	10	-24	1169.32400	35	-4	12	12	0	1330.20136	17	-19	1543.26697	5	21	1398.81241	19	-11
8	7	1	1099.70264	17	-12	1309.71381	19	7	1178.67017	16	14	12	12	1	1330.24294	16	-24	1543.27224	10	16	1398.81660	17	-10
8	7	2	1101.92975	19	7	1310.85635	17	2	1179.78086	14	12	12	11	1	1338.63548	14	1	1555.29145	7	15	1414.38113	19	-10
8	6	2	1103.27125	6	-8	1314.08974	13	10	1184.66218	18	17	12	11	2	1339.43909	19	-1	1555.46441	14	8	1414.51200	12	-41
8	6	3	1109.27074	20	6	1318.59861	18	5	1189.66005	18	17	12	10	2	1344.01370	3	-22	1564.22028	10	-4	1426.65012	20	18
8	5	3	1109.40417	13	10	1319.26095	24	9	1190.87761	40	-2	12	10	3	1347.95864	13	4	1565.93970	29	14	1428.14520	17	8
8	5	4	1118.98093	10	24	1327.91284	18	3	1201.16352	13	-2	12	9	3	1349.20596	15	-42	1570.13524	14	- 9	1434.84729	16	12
8	4	4	1118.98554	12	35	1327.95735	18	12	1201.26885	17	-7	12	9	4	1357.70805	13	-8	1576.08120	17	-16	1440.99375	20	14
8	4	5	1131.51649	14	16	1339.78110	12	26	1215.70282	20	0	12	8	4	1357.82787	19	-23	1577.01376	13	-31	1442.92355	30	-12
8	3	5	1131.51649	14	9	1339.78212	29	4	1215.70685	7	7	12	8	5	1370.00720	10	-5	1587.79795	14	-16	1455.28871	15	-12
8	3	6	1146.92844	26	15	1354.35700	15	20	1233.57805	26	14	12	7	5	1370.01237	5	7	1587.87754	13	-41	1455.51656	22	-19
8	2	6	1146.92844	26	15	1354.35700	15	19	1233.57805	26	6	12	7	6	1385.18923	15	9	1602.12833	9	-38	1472.56732	17	-14
8	2	7	1165.24070	10	2	1371.61999	17	27	1254.78785	17	4	12	6	6	1385.18923	15	9	1602.13175	22	-27	1472.58087	12	-17
8	1	7	1165.24070	10	2	1371.61999	17	27	1254.78785	17	4	12	6	7	1403.27886	22	-38	1619.24033	15	-30	1493.20948	19	20

[a] In Table 6, Δ is the experimental uncertainty of the energy value, equal to one standard deviation in units of 10^{-5} cm^{-1}; δ is the difference $E^{exp.} - E^{calc.}$, also in units of 10^{-5} cm^{-1}; Δ is not quoted when the energy value was obtained from only one transition.

TABLE 6—*Continued*

			(000100)			(001000)			(000001)						(000100)			(001000)			(000001)		
J	K_a	K_c	E	Δ	δ	E	Δ	δ	E	Δ	δ	J	K_a	K_c	E	Δ	δ	E	Δ	δ	E	Δ	δ
	1		2	3	4	5	6	7	8	9	10		1		2	3	4	5	6	7	8	9	10
12	5	7	1403.27886	22	16	1619.24033	15	-37	1493.20948	19	-28	15	8	8	1661.82485	14	-15	1885.81675	6	-28	1755.33881	35	7
12	5	8	1424.29238	23	-54	1639.09945	7	-28	1517.19996	13	13	15	7	8	1661.81420	17	-7	1885.81675	6	-34	1755.33881	35	-40
12	4	8	1424.29238	23	27	1639.09945	7	-28	1517.19996	13	12	15	7	9	1685.50562		-26	1908.25920	10	-12	1782.07409	13	-10
12	4	9	1448.25996	11	-15	1661.67396	8	-6	1544.51597	20	28	15	6	9	1685.52855	5	-2	1908.25920	10	-12	1782.07409	13	-21
12	3	9	1448.25996	11	-8	1661.67396	8	-6	1544.51597	20	28	15	6	10	1712.25535	8	21	1933.46602	11	17	1812.12876	20	-38
12	3	10	1475.21478	6	-16	1686.93454	2	23	1575.16476	15	20	15	5	10	1712.22255	5	12	1933.46602	11	17	1812.12876	20	-22
12	2	10	1475.21478	6	-16	1686.93454	2	23	1575.16476	15	20	15	5	11	1741.87473	10	-9	1961.41200	6	-10	1845.45344	12	-31
12	2	11	1505.19698	13	-17	1714.83560	10	26	1609.18325	15	-6	15	4	11	1741.87473	10	-9	1961.41200	6	-10	1845.45344	12	-30
12	1	11	1505.19698	13	-17	1714.83560	10	26	1609.18325	15	- 6	15	4	12	1774.59924	12	-8	1992.08250	12	19	1882.13266	28	-39
12	1	12	1538.24853	6	2	1745.28457	1	-30	1646.64273	3	-52	15	3	12	1774.59924	12	-8	1992.08250	12	19	1882.13266	28	-39
12	0	12	1538.24853	6	2	1745.28457	1	-30	1646.64273	3	-52	15	3	13	1810.40333	13	9	2025.41594	40	-1	1922.18673	30	-36
13	13	0	1402.70009	17	-25	1617.35582	6	16	1469.68753	16	-7	15	2	13	1810.40333	13	9	2025.41594	40	-1	1922.18673	30	-36
13	13	1	1402.72501	10	-19	1617.35837	12	9	1469.69020	26	-5	15	2	14	1849.37466	6	5	2061.28423		-10	1965.71706	28	66
13	12	1	1412.17512	11	0	1630.60689	8	-4	1486.67090	18	-5	15	1	14	1849.37466	6	-12	2061.28423		-10	1965.71706	28	66
13	12	2	1412.73962	12	2	1630.70450	18	1	1486.74189	24	-12	15	1	15	1891.49894		5	2099.32548	4	33			
13	11	2	1418.39310	11	-15	1640.93291	13	-7	1500.61988	11	-1	15	0	15	1891.49894		5	2099.32548	4	33			
13	11	3	1421.73344	19	-13	1642.11884	13	-18	1501.57780	22	-13	16	16	0	1653.02110	10	19	1872.87607		-10	1714.67085		-2
13	10	3	1423.58097	6	-20	1647.71143	-	-5	1510.22830	25	-17	16	16	1	1653.02549	15	-12	1872.87607		-4	1714.71601		8
13	10	4	1431.57359	4	5	1652.72494	12	-9	1515.12604	15	-16	16	15	1	1665.57522	6	-9	1889.78560	12	-5	1735.74521	8	0
13	9	4	1431.79822	13	-20	1654.29957	12	-25	1518.22278	9	-22	16	15	2	1665.73576	6	-14	1889.80073	2	-2	1735.76856	8	-19
13	9	5	1443.79914	17	11	1664.47363	13	-30	1529.52373	9	-30	16	14	2	1674.93646	18	28	1904.13191		-26	1754.25907	19	42
13	8	5	1443.81067	1	4	1664.64670	14	-46	1529.99971	14	-16	16	14	3	1676.59430	20	-23	1904.42493		-58	1754.47853	22	36
13	8	6	1458.89640	6	6	1678.70575	16	-53	1546.62913	13	-40	16	13	3	1681.12864	8	69				1769.08682	18	6
13	7	6	1458.89640	6	10	1678.71500	48	-24	1546.66449	20	-30	16	13	4	1687.06644	22	-14				1770.89545	19	1
13	7	7	1476.90848	5	-3	1695.73764		-48	1567.07597		-20	16	12	4	1688.12437		-30				1779.29811	16	58
13	6	7	1476.90764	12	14	1695.73786		-51	1567.07756		-17	16	12	5	1699.11713	18	-44				1786.40214		-34
13	6	8	1497.84343	62	-117	1715.54561	13	-38	1590.88627	16	4	16	11	5	1699.21565		31				1789.04071		98
13	5	8	1497.84343	62	88	1715.54561	13	-38	1590.88627	16	-1	16	11	6	1713.88590	26	-57				1803.22452	31	-79
13	5	9	1521.73162	23	-34	1738.09319	15	-28	1618.02291	14	18	16	10	6	1713.84686	25	-6				1803.59226	14	38
13	4	9	1521.73162	23	17	1738.09319	15	-28	1618.02291	14	18	16	10	7	1731.59430	14	-47				1822.96063		105
13	4	10	1548.60003	15	-19	1763.35414	14	14	1648.48131	15	18	16	9	7	1731.58131	4	-14				1822.98868	30	65
13	3	10	1548.60003	15	-19	1763.35414	14	14	1648.48131	15	18	16	9	8	1752.23808	11	-46						
13	3	11	1578.48915	9	-22	1791.29412	9	2	1682.27891	10	-19	16	8	8	1752.21343	14	-18						
13	2	11	1578.48915	9	-22	1791.29412	9	2	1682.27891	10	-19	16	8	9	1775.82282	13	-9				1872.61768	30	78
13	2	12	1611.44091	7	-14	1821.85130	18	8	1719.47568	10	-13	16	7	9	1775.84078	5	6				1872.61768	30	60
13	1	12	1611.44091	7	-14	1821.85130	18	8	1719.47568	10	-13	16	7	10	1802.38095	22	30				1902.45509		42
13	1	13	1647.49634	6	4	1854.88222	6	-39	1760.16760	12	-46	16	6	10	1802.37534		80				1902.45509		62
13	0	13	1647.49634	6	4	1854.88222	6	-39	1760.16760	12	-46	16	6	11	1831.95196	7	-31				1935.52476		47
14	14	0	1480.67857	12	-10	1696.99934		-5	1545.95725	20	8	16	5	11	1831.95196	7	-31				1935.52476		47
14	14	1	1480.69305	10	-18	1697.00076	13	8	1545.95991	4	11	16	5	12	1864.54830	31	-14				1971.94881	28	0
14	13	1	1491.18668	18	-4	1711.46968	32	-17	1564.32570	11	5	16	4	12	1864.54830	31	-14				1971.94881	28	0
14	13	2	1491.56950	10	35	1711.52325	15	-15	1564.36480	17	-2	16	4	13	1900.21112	11	16				2011.69973	18	20
14	12	2	1498.37198	25	-10	1723.17556	19	-12	1579.87299	16	-2	16	3	13	1900.21112	11	16				2011.69973	18	20
14	12	3	1501.11344	36	12	1723.95218	6	-55	1580.46062	7	-20	16	3	14	1939.05864	11	-4						
14	11	3	1503.71239	13	-7	1731.07765		-32	1591.13928	18	-15	16	2	14	1939.05864	11	-4						
14	11	4	1511.09734	15	1	1735.14345		12	1594.85144	23	-35	16	2	15	1981.02484	15	23						
14	10	4	1511.49485	15	-10	1737.60407		0	1599.44142	10	-17	16	1	15	1981.02484	15	23						
14	10	5	1523.25154	11	-6	1746.99139	34	18	1609.47328		-40	16	1	16	2026.21499	5	-7						
14	9	5	1523.27653	6	0	1747.33837		-39	1610.38577	19	-9	16	0	16	2026.21499	5	-7						
14	9	6	1538.25170	12	-6	1761.12942	8	-43	1626.42333	11	-47	17	17	0	1747.35482		50	1969.06930		-11	1807.10888		-24
14	8	6	1538.25170	12	24	1761.14960		32	1626.50686	22	-33	17	17	1	1747.35690		1	1969.06930		18	1807.08673		-1
14	8	7	1556.17501	7	-7	1778.05074	41	-7	1646.65533	30	-14	17	16	1	1760.93181	9	-20	1987.20681		12			
14	7	7	1556.17274	10	-4	1778.05074	41	-84	1646.65973	15	-23	17	16	2	1761.03167	9	-31	1987.21438		96			
14	7	8	1577.02425	3	-6	1797.78861	13	4	1670.26549	17	-4	17	15	2	1771.42715	8	1	2002.82154		-1			
14	6	8	1577.01954	1	0	1797.78861	13	2	1670.26549	17	-2	17	15	3	1772.64454		-55	2002.99244	18	-36			
14	6	9	1600.82817	11	-10	1820.29292	17	-26	1697.20895	12	-6	17	9	9	1871.72796		-15						
14	5	9	1600.82311	3	-6	1820.29292	17	-26	1697.20895	12	-7	17	8	9	1871.75232		8						
14	5	10	1627.59849	15	-19	1845.53621	9	17	1727.46959	13	-17	17	8	10	1898.16797		89						
14	4	10	1627.59819	15	-31	1845.53621	9	17	1727.46959	13	-18	17	6	11	1927.60789		-68						
14	4	11	1657.38433	11	-16	1873.49189	18	-13				17	6	12	1960.06550		-32						
14	3	11	1657.38433	11	-16	1873.49189	18	-13	1761.02763	12	-38	17	5	12	1960.06550		-32						
14	3	12	1690.22726	16	-10	1904.12114	24	-39	1797.97378	12	-40	17	5	13	1995.57720		14						
14	2	12	1690.22726	16	-10	1904.12114	24	-39	1797.97378	12	-40	17	4	13	1995.57720		14						
14	2	13	1726.16245	7	-3	1937.33342	3	-59	1838.34006	21	-25	17	3	15	2076.09298		0						
14	1	13	1726.16245	7	-3	1937.33342	3	-59	1838.34006	21	-25	17	2	15	2076.09298		0						
14	1	14	1765.25479		-4	1972.90361	3	-12	1882.27319	56	92	17	2	16	2121.10873		18						
14	0	14	1765.25479		-4	1972.90361	3	-12	1882.27319	56	92	17	1	16	2121.10873		18						
15	15	0	1564.12371	10	1	1782.17941	13	1	1627.61932	8	20	17	1	17	2169.38199		-11						
15	15	1	1564.13189	13	-15	1782.17941	13	-50	1627.62465	7	12	17	0	17	2169.38199		-11						
15	14	1	1575.65690	9	2	1797.86751		-34	1647.35008	9	17	18	18	0	1847.10741	32	110	2070.74784		-52	1904.93331		-44
15	14	2	1575.90826	12	-7	1797.89609		46	1647.37442	5	3	18	18	1	1847.10741	32	-31	2070.73911		-84	1904.91162		3
15	13	2	1583.90292	29	44	1810.91388	6	-23	1664.41395	8	10	18	17	1	1861.71537	9	-7						
15	13	3	1586.07510	20	-18	1811.39990	13	-56	1664.76679	16	10	18	17	2	1861.77600	16	-21						
15	12	3	1589.57352	25	12	1820.13879		46	1677.45870	5	-27	19	19	0	1952.25865	22	76	2177.86270	89	134	2008.16538		-36
15	12	4	1596.26716	21	16	1823.29451	21	43	1680.12382	8	-7	19	19	1	1952.25865	22	1	2177.86270	89	2	2008.11016		43
15	11	4	1596.93277		5	1826.88594		58	1686.52651	21	22	19	18	1	1967.91254	20	90						
15	11	5	1608.35986	19	-11	1835.32873	14	64	1695.11114	14	-48	20	20	0	2062.78872	15	38	2290.42268	78	147	2116.68447		-20
15	10	5	1608.41063	16	3	1835.97636	37	11	1696.72422	15	15	20	20	1	2062.78872	15	-1	2290.42268	78	49	2116.54985		82
15	10	6	1623.25036	16	0	1849.36075	8	34	1711.92777	28	-62	21	21	0	2178.67474		-50	2408.39551		-5			
15	9	6	1623.24833	17	17				1712.07844	17	-21	21	21	0	2178.67474		-70	2408.39551		-97			
15	9	7	1641.07269	11	-8				1731.94926	30	-42	22	22	0	2299.89468		22						
15	8	7	1641.06770	14	12				1731.96130	9	-11	22	22	1	2299.89468		11						

TABLE 7
Parameters of Resonance Interactions for the (000100), (001000), and (000001) Vibrational States of the PH_2D Molecule (in cm^{-1})

Coriolis-type interactions

Parameter	Value	Parameter	Value	Parameter	Value
$(2B\zeta^x)^{1-2}$	-4.1498(898)	$C_{xK}^{1-2} \times 10^3$	-0.36994(662)	$C_{xJ}^{1-2} \times 10^3$	0.78534(892)
$C_{yz}^{1-2} \times 10$	-0.61276(226)	$C_{yzJ}^{1-2} \times 10^4$	0.35560(786)	$C_{yzKK}^{1-2} \times 10^7$	0.4914(118)
$(2C\zeta^y)^{1-3}$	3.1775(303)	$C_{yK}^{1-3} \times 10^3$	-0.41559(669)	$C_{yJ}^{1-3} \times 10^3$	-0.28308(128)
$C_{yKK}^{1-3} \times 10^6$	-0.5540(219)	$C_{yJK}^{1-3} \times 10^6$	1.5522(199)	$C_{yKKK}^{1-3} \times 10^9$	1.5088(457)
$C_{xz}^{1-3} \times 10$	0.24131(568)	$C_{xzK}^{1-3} \times 10^4$	-0.04933(207)	$C_{xzJ}^{1-3} \times 10^4$	0.22143(711)
$C_{xzKK}^{1-3} \times 10^7$	0.09681(775)	$C_{xzJK}^{1-3} \times 10^7$	0.2484(127)	$C_{xzJJ}^{1-3} \times 10^7$	-0.8873(167)
$C_{zK}^{1-3} \times 10^3$	0.6237(136)				
$(2A\zeta^z)^{2-3}$	3.0321(538)	$C_{zK}^{2-3} \times 10^3$	-0.19381(332)	$C_{zJ}^{2-3} \times 10^3$	0.12408(302)
$C_{zKK}^{2-3} \times 10^6$	0.7019(163)	$C_{zJJ}^{1-3} \times 10^6$	-0.5559(156)	$C_{zKKK}^{2-3} \times 10^9$	-0.1659(140)
$C_{xy}^{2-3} \times 10$	0.10904(102)	$C_{xyK}^{2-3} \times 10^4$	0.37018(590)	$C_{xyJ}^{2-3} \times 10^4$	-0.38761(576)
$C_{xyKK}^{2-3} \times 10^7$	0.4596(226)	$C_{xyJK}^{2-3} \times 10^7$	-1.4029(248)	$C_{xyJJ}^{2-3} \times 10^7$	0.52239(837)
$C_{yK}^{2-3} \times 10^3$	-1.0444(350)	$C_{yJ}^{2-3} \times 10^3$	0.35368(580)	$C_{yKK}^{2-3} \times 10^6$	-2.966(128)
$C_{yJK}^{2-3} \times 10^6$	2.210(124)	$C_{xzK}^{2-3} \times 10^4$	0.09313(512)	$C_{xzJ}^{2-3} \times 10^4$	-0.7781(108)
		$C_{xzKK}^{2-3} \times 10^7$	0.4286(106)		

Fermi-type interactions

Parameter	Value	Parameter	Value	Parameter	Value
F_0^{1-2}	-14.263(486)	$F_K^{1-2} \times 10^2$	-4.5818(580)	$F_J^{1-2} \times 10^2$	2.7365(294)
$F_{KK}^{1-2} \times 10^4$	0.7260(118)	$F_{JK}^{1-2} \times 10^4$	-0.5618(107)	$F_{KKK}^{1-2} \times 10^7$	-0.93111(699)
$F_{KJJ}^{1-2} \times 10^7$	1.081(706)	$F_{xy}^{1-2} \times 10^2$	4.4567(203)	$F_{xyK}^{1-2} \times 10^4$	0.20449(615)
$F_{xyJ}^{1-2} \times 10^4$	0.03248(176)	$F_{xyKK}^{1-2} \times 10^6$	-0.03519(236)	$F_{xyJK}^{1-2} \times 10^6$	-0.11845(209)

[a] See footnote to Table 4.

5 (ν_3), and 8 (ν_6) together with their experimental uncertainties Δ (columns 3, 6, and 9, respectively). It should be said that really the number of assigned transitions was a little bit larger than it is mentioned above. However, we used in the fit only the upper energies determined from the doubtlessly assigned lines.

It has been noted in the previous study (*10*) of the ν_3, ν_4, and ν_6 triad that, owing to correlation effects, the fit was unstable, rotational and Coriolis constants drastically changing, the latter also being dependent on the chosen reduction (*10*). In order to circumvent correlation problems we chose a different approach. Based on the experience that centrifugal distortion constants of excited states should be close to the ground state values we varied in the first step of our data fit only the band centers and the rotational constants. The centrifugal distortion constants were constrained to their ground state values. At the same time many

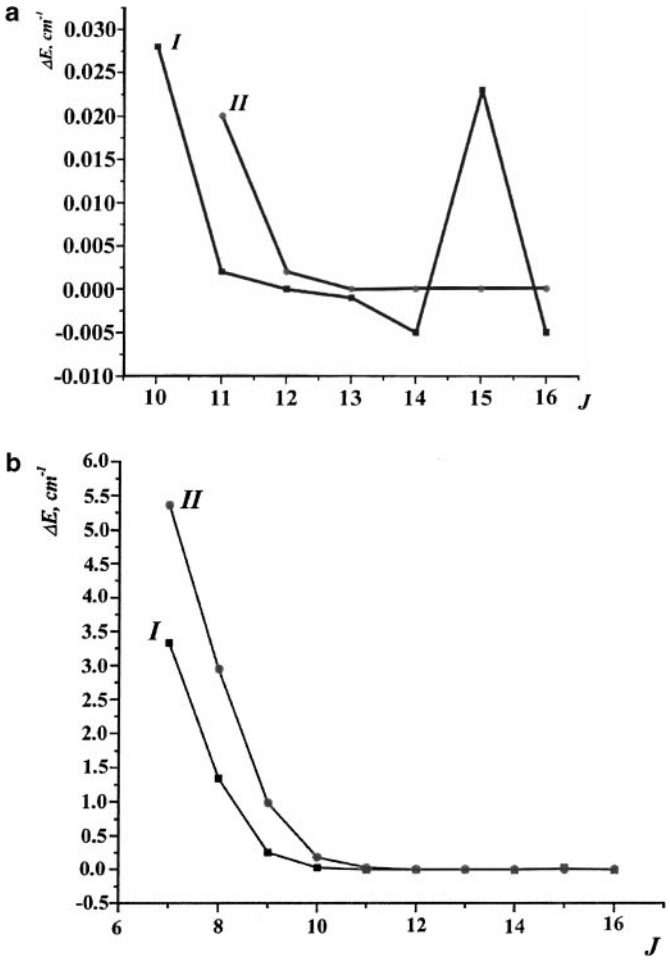

FIG. 5. Diagram of the dependence of the value $\Delta_J = E_{J\,K_a=6\;K_c=J-6} - E_{J\;K_a=7\;K_c=J-6}$ on the value of the quantum number J. Trace I corresponds to the vibrational state ($v_4 = 1$). In this case, (a) shows in more detail the part of the general diagram; (b) concerns high values of the quantum number J. The unusual behavior of trace I is caused by the presence of strong resonance interactions of the states $[JK_a = 6\,K_c = J - 6](v_6 = 1)$ and $[JK_a = 7\,K_c = J - 6](v_4 = 1)$ with different states $[JK_a\;K_c](v_4 = 1)$. For comparison, diagram II shows the usual behavior of the value $\Delta_J = E_{J\;K_a=6\;K_c=J-6} - E_{J\;K_a=7\;K_c=J-6}$ versus the value of the quantum number J for the ground vibrational state.

interaction parameters were refined. This was compulsory because resonance interactions are numerous and strong. One such resonance interaction is illustrated in Fig. 5 where for the $v_4 = 1$ (trace I) and the ground state (trace II) the energy difference $\Delta_J = E_{JK_a=6K_c=J-6} - E_{JK_a=7K_c=J-6}$ is displayed for different J.

One more strong resonance interaction that became detectable thanks to the superior resolution of the present spectra is the splitting of the energy cluster $[J = 18K_a = 18K_c = 1]/[J = 18K_a = 18K_c = 0]$ of the vibrational state $v_3 = 1$. Table 6 illustrates that the clusters $[JK_a = JK_c = 1]/[JK_a = JK_c = 0]$ $(v_3 = 1)$, both with the smaller and larger quantum numbers J, are unsplit while the $J = 18$ cluster is split because of its strong interaction with the $[J = 18K_a = 13K_c = 5]/[J = 18K_a = 13K_c = 6]$ $(v_6 = 1)$ states. The corresponding doublet at 1113.41342 and 1113.42220 cm^{-1} is found in the Q branch of the v_3 band, and both transition wavenumbers are correctly predicted by our model. This doublet was not resolved in Ref. (*10*).

In the final step the centrifugal distortion constants Δ_K, Δ_{JK}, and Δ_J were also refined while all other centrifugal distortion constants up to octic terms were constrained to their ground state values. The excited state molecular parameters for the triad are reported in Table 4 and the interaction constants are given in Table 7. Altogether 21 molecular parameters and 50 interaction constants, in total 71 parameters, were refined. This may be compared with $36 + 24 = 60$ and $35 + 20 = 55$ parameters in sets 1 and 2 of Ref. (*10*). The larger number of parameters needed in the present study is required, above all, by the higher quantum numbers of the probed energy levels and the higher precision of the data. This latter criterium can be assessed by the δ values given in columns 4, 7, and 10 of Table 6, which quote the differences in units of 10^{-5} cm^{-1} between experimental energies and those calculated with the parameters of Tables 4 and 7.

The Coriolis interaction constants and the rotational–vibrational constants $\alpha_\lambda^{\prime\beta}$ ($\beta = x, y, z$ and $\lambda = 3, 4$, and 6) shown in column 3 of Table 3 may be compared with the predictions outlined in Section 2. Most of them are in reasonable agreement. This agreement is particularly noteworthy in view of the fact that PH_3 is not a "true local mode" molecule, the equilibrium interbond angle being near 93.5° rather than 90°, and the m_H/M_P ratio is close to 1/31.

A further criterion for the physical significance of our model is the closeness of the final, refined excited state quartic centrifugal distortion constants Δ_K, Δ_{JK}, and Δ_J with regard to those of the ground state. While our Δ difference values are on average 1.9% in absolute value and do not exceed 3.9%, the average/maximum D differences in Ref. (*10*) are much larger both in Model 1 and Model 2: 9.5/23.2 and 18.9/27.2%, respectively. The averaged absolute values of the D constants are about the same in Ref. (*10*) as the Δ values in the present study in spite of the different representation used. Also the excited state d_1 and d_2 values in Model 2 (*10*) differ substantially from the ground state values.

6. CONCLUSION

For ${}^M X^m Y_3$, C_{3v} symmetry molecules satisfying the abovementioned local mode conditions, isotopic relations for the rotation–vibration α_λ^β, and quartic centrifugal distortion parameters were derived for the case where one of the light atoms Y is replaced (here H by D). Our results were successfully tested for the assignment and the fit of a new high-resolution Fourier transform spectrum of PH_2D in the region of the three lowest vibrational–rotational bands v_4, v_6, and v_3. The analysis benefitted from the precise, improved rotational energies of the ground vibrational state. This fact, on the one hand, and the higher resolution and higher sensitivity than in an earlier contribution (*10*) on the other hand, enabled us to assign transitions with higher values of quantum number J and to achieve higher accuracy in the values of rotation–vibration energies in the upper states

than in the earlier study. The fit of the obtained upper state energies in the framework of Watson's A-reduced Hamiltonian in III^l representation leads to a physically meaningful set of 71 spectroscopic parameters which reproduce the 881 observed "experimental" energies with accuracies close to the experimental precision. It is to be expected that our approach to predicting parameters of isotopically substituted "daughter" species from those of the "mother" molecule will likewise be successful for other vibrations of PH_2D. Supposedly this method will be even more powerful if the target molecules fulfill local mode conditions better than PH_3 and PH_2D, as is the case for H_2Se and HDSe, which were studied earlier (*1*, *2*).

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