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NON-EMPIRICAL ANHARMONIC ANALYSIS OF VIBRATIONAL STATES OF BF_3 AND BH_3 USING SYMMETRY COORDINATES

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Force fields, anharmonic constant matrices, and harmonic and anharmonic frequencies of vibrational states of BF_3 and BH_3 were calculated using B3LYP/cc-pVTZ/cc-pVQZ/cc-pV5Z/acc-pV5Z approximations. Anharmonic IR spectra of the molecules were calculated by the vibrational self-consistent field (VSCF) method included in the quantum chemistry package GAMESS. Frequencies of totally symmetric stretching vibrations were refined by constructing potential surfaces using symmetry coordinates. The Schroedinger equation transformed into symmetry coordinates was solved numerically using construction followed by diagonalization of the Hamiltonian matrix. It was shown that the last approach reproduced the experimental vibrational frequencies for BF_3 more accurately than those obtained in the anharmonic approximation. The frequencies of the totally symmetric stretching vibration of BH_3, which is especially interesting because of the lack of experimental data, that were calculated in the harmonic and anharmonic approximations and by constructing potential surfaces were 2565, 2503, and 2539 cm^{-1}, respectively.

Keywords: *force field, vibrational spectrum, potential energy surface, symmetry coordinates, Hamiltonian matrix.*

Introduction. Borane (BH_3) is the simplest boron hydride. Boron hydrides are electron-deficient compounds, i.e., they lack enough electrons to bind all atoms by ordinary two-electron bonds. For example, BH_3 has a total of six valence electrons. It is planar in the singlet ground state and belongs to symmetry group D_{3h}. It is rather difficult to observe BH_3 because it quickly dimerizes into the more stable compound diborane (B_2H_6). The B atoms in B_2H_6 are bonded to H atoms through ordinary bonds. However, the B atoms are bonded through three-center "bridging" bonds. Despite the fact that BH_3 is known only in complexes, e.g., with amines, its transient existence was postulated in order to explain many chemical reactions involving boron hydrides. The high reactivity of BH_3 hinders observation of its gas-phase spectrum. Hence, there is a problem with observing electronic transitions because the excited electronic states that are attainable from the ground state can be dissociative. The IR spectrum of BH_3 was first reported only in 1971 because of its instability [1]. Several proposed assignments [1] were disputed in later experimental studies [2, 3]. The Raman spectrum of this molecule has not been published. These facts emphasize the need for theoretical investigations of this molecule, especially its totally symmetric vibrations that are inactive in the IR spectrum. The BH_3 molecule is well suited for theoretical calculations because of its small size. Its structure and vibrational spectra were the subjects of many theoretical investigations [4–7]. However, they all were performed in a harmonic approximation despite the fact that involvement of the light H atom in BH_3 vibrations suggests that anharmonism effects should appear.

BF_3, in contrast with BH_3, is one of several stable XY_3 gases with D_{3h} symmetry and the subject of many spectral investigations. Both IR and Raman spectra of this compound were reported [8–21]. Therefore, BF_3 can be considered a "touchstone" for methods used to calculate theoretically BH_3 vibrational spectra.

Group Analysis of BF_3 and BH_3 Molecular Vibrations. BH_3 and BF_3 (Fig. 1) have point-group symmetry D_{3h}. Six of its vibrations are represented by the following symmetry types:

$$\Gamma_\upsilon = 1A_1' + 1A_2'' + 2E'.$$

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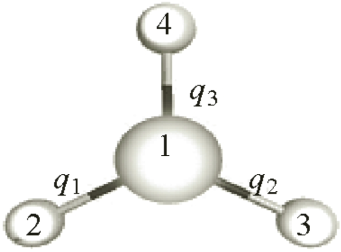

Fig. 1. Molecular configuration of BH_3 and BF_3 with atomic numbering and bond coordinate numbers.

Figure 1 shows that the only totally symmetric vibration was related to B–X, where X = H or F, stretching coordinates. Thus, the totally symmetric B–X stretching vibrations cannot be mixed with other in-plane and/or out-of-plane molecular coordinates. Of the three symmetry types represented in Γ_υ, only A_2'' is asymmetric relative to the horizontal symmetry plane. Therefore, the out-of-plane B–X bending vibration belongs to this type. Obviously, it also does not mix with another type of coordinates. The two degenerate E' vibrations are asymmetric stretching and in-plane bending B–X vibrations. Although the energies of these vibrations differ, they can be partially mixed. Vibrations of the A_1' and E' types are active in the Raman spectrum; A_2'' and E', in the IR spectrum. Thus, only four fundamental vibrations of different frequency can occur in BH_3 and BF_3 vibrational spectra. The aforementioned also indicates that experimental data on the frequency of the totally symmetric B–H stretching vibration in BH_3 are missing.

Calculations. The geometry, harmonic and anharmonic vibrational spectra, and potential surfaces (1D potential energy surfaces, 1D-PES) of BH_3 and BF_3 were calculated using the GAMESS quantum-chemical package [22] using density functional theory DFT/B3LYP [23] for basis set cc-pVTZ [24]. Anharmonic IR spectra were calculated using a vibrational self-consistent field (VSCF) method [25]. The structure and vibrational spectra of BH_3 were also calculated using basis sets cc-pVQZ, acc-pVQZ, cc-pV5Z, and acc-pV5Z [24]. 1D-PES for B–X stretching vibrations were constructed using symmetry coordinates:

$$q_1^{\mathrm{s}} = (q_1 + q_2 + q_3)\big/\sqrt{3}\ , \qquad q_2^{\mathrm{as}} = (2q_1 - q_2 - q_3)\big/\sqrt{6}\ , \qquad q_3^{\mathrm{as}} = (q_2 - q_3)\big/\sqrt{2}\ . \tag{1}$$

For a molecule with the geometry shown in Fig. 1 and for which all natural coordinates except stretching ones are fixed, the Hamiltonian can be written:

$$G_{11}\frac{\partial^2}{\partial q_1^2} + G_{22}\frac{\partial^2}{\partial q_2^2} + G_{33}\frac{\partial^2}{\partial q_3^2} + 2G_{12}\frac{\partial^2}{\partial q_1 \partial q_2} + 2G_{13}\frac{\partial^2}{\partial q_1 \partial q_3} + 2G_{23}\frac{\partial^2}{\partial q_2 \partial q_3} + U(q_1, q_2, q_3)\ , \tag{2}$$

where according to the literature [26]:

$$G_{11} = G_{22} = G_{33} = -\hbar^2/2\mu_{\mathrm{BX}} = -\,\hbar^2(M_{\mathrm{B}} + M_{\mathrm{X}})/2M_{\mathrm{B}}M_{\mathrm{X}}\,, \tag{3}$$

$$G_{12} = G_{13} = G_{23} = -\,\hbar^2\cos\theta/2M_{\mathrm{B}} = \{\theta = 2\pi/3\} = +\,\hbar^2/4M_{\mathrm{B}}\,.$$

Using Eqs. (1)–(3), we obtain

$$\widehat{H}^{\mathrm{s}} = -\frac{\hbar^2}{2M_{\mathrm{X}}}\frac{\partial^2}{\partial q_1^{\mathrm{s}2}} + U(q_1^{\mathrm{s}})\ , \tag{4}$$

$$\widehat{H}_2^{\mathrm{as}} = -\frac{\hbar^2}{2}\,\frac{2M_{\mathrm{B}} + 3M_{\mathrm{X}}}{2M_{\mathrm{B}}M_{\mathrm{X}}}\,\frac{\partial^2}{\partial q_2^{\mathrm{as}2}} + U(q_2^{\mathrm{as}}), \tag{5}$$

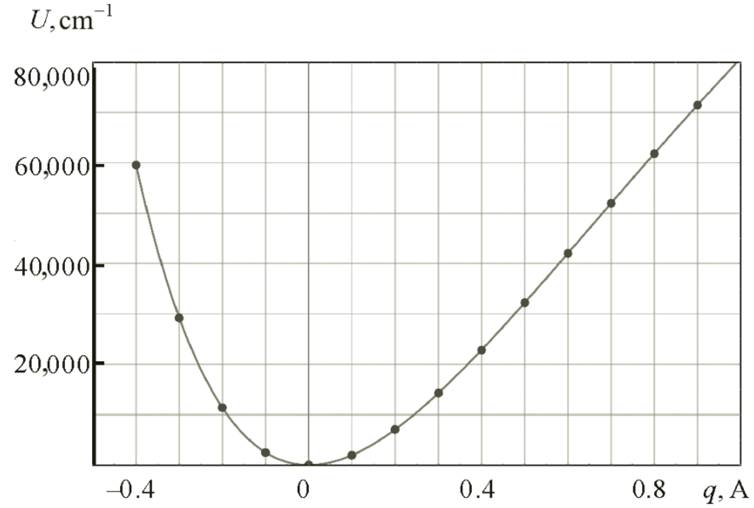

Fig. 2. Calculated PES for symmetric vibration $\nu_{\mathrm{BF}}^{A_1'}$.

$$\widehat{H}_3^{\mathrm{as}} = -\frac{\hbar^2}{2}\frac{2M_{\mathrm{B}}+3M_{\mathrm{X}}}{2M_{\mathrm{B}}M_{\mathrm{X}}}\frac{\partial^2}{\partial q_3^{\mathrm{as}2}} + U(q_3^{\mathrm{as}})\,. \qquad (6)$$

Despite the fact that Eqs. (5) and (6) appear fully identical, their potential energies are considerably different. According to Eq. (1) and the equivalency of stretching coordinates q_1, q_2, and q_3, the function $U(q_3^{\mathrm{as}})$ should be symmetric relative to the ordinate axis whereas $U(q_2^{\mathrm{as}})$ does not satisfy this requirement. Potential surfaces were calculated in 0.1 Å steps with a coordinate variation interval of 1.5 Å. Schroedinger equations with Hamiltonian operators of the types in Eqs. (4)–(6) were solved numerically. The solution method was reported before [27, 28].

The use of symmetry coordinates seemed interesting because rather than constructing 3D-PES if natural coordinates q_1, q_2, and q_3 were used, it was sufficient to construct three 1D-PES in order to determine the B–X stretching frequencies. For this, their anharmonism was fully considered and computational losses were significantly economized. In fact, assuming that calculating the energy at 15 points for a single degree of freedom was sufficient to attain the required accuracy, the system energy at 15^3 (3375) points had to be calculated to construct 3D-PES whereas a total of 45 points had to be calculated for the three 1D-PES.

Calculation of BF$_3$ Vibrational States. We used standard designations for BH$_3$ and BF$_3$ vibrations: $\nu_{\mathrm{BX}}^{A_1'}$, $\nu_{\mathrm{BX}}^{E'}$, $\delta_{\mathrm{XBX}}^{E'}$, $\delta_{\mathrm{XBX}}^{A_2''}$. Obviously, the amplitudes of BF$_3$ vibrations were small so that it could be assumed that the calculated harmonic vibrational frequencies would agree well with the experimental values. The adequacy of the 1D-calculations of the vibrational energy levels could also be checked using symmetry coordinates to construct the PES. Figures 2 and 3 show 1D-PES for symmetry coordinates q_1^{s}, q_2^{as}, and q_3^{as}.

As noted earlier, the function $U(q_3^{\mathrm{as}})$ (Fig. 3a) was symmetric relative to the ordinate axis whereas $U(q_2^{\mathrm{as}})$ and especially $U(q_1^{\mathrm{s}})$ were asymmetric relative to this axis. Table 1 lists BF$_3$ vibrational frequencies that were calculated in harmonic and anharmonic approximations and also using symmetry coordinates to construct 1D-PES.

It is noteworthy that the $\nu_{\mathrm{BX}}^{A_1'}$ values (887 cm^{-1}) calculated using 1D-PES agreed excellently with the experimental ones (888 cm^{-1}) and those obtained in the harmonic approximation (889 cm^{-1}). The frequency of this vibration that was calculated in the anharmonic approximation (866 cm^{-1}) was considerably less than the experimental value. This confirmed the known tendency to overestimate anharmonism of vibrations when calculating it using the standard model and second-order perturbation theory [29]. It is noteworthy that the discrepancy in the $\nu_{\mathrm{BX}}^{E'}$ value estimated using 1D-PES and that obtained experimentally was due mainly to mixing of stretching and bending coordinates of the same symmetry in this type of vibration. This was not taken into account in calculations using PES construction. In fact, the fraction of B–F stretching coordinates was 100% in the potential energy distribution (PED) of the $\nu_{\mathrm{BX}}^{E'}$ vibration whereas the fraction of stretching coordinates was 93% in the PED of the $\nu_{\mathrm{BX}}^{A_1'}$ vibration; the fraction of F–B–F in-plane bending coordinates, 7%.

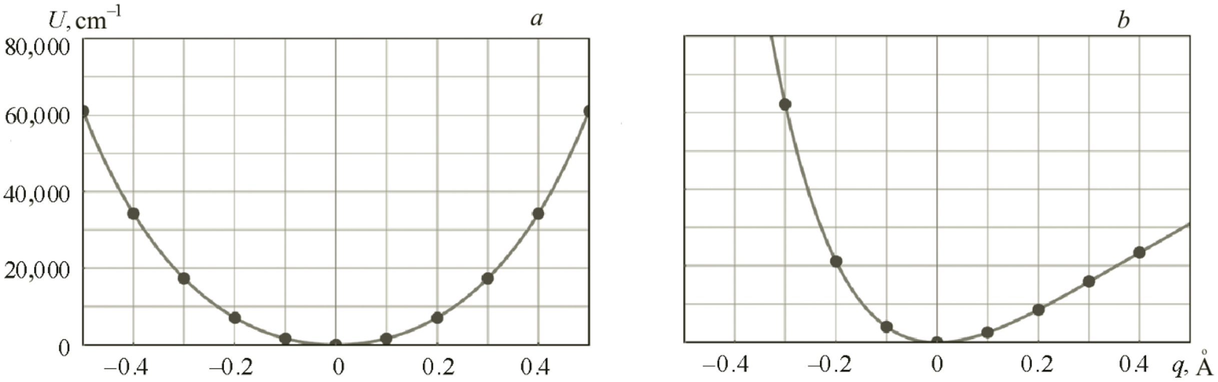

Fig. 3. Calculated PES for asymmetric vibration $\nu_{\mathrm{BX}}^{E'}$ related to the coordinate change for q_3^{as} (a) and q_2^{as} (b).

TABLE 1. Calculated and Experimental Frequencies (ν, cm^{-1}) of BF$_3$ Fundamental Vibrations

Mode	B3LYP/cc-pVTZ		B3LYP/cc-pVTZ	ν_{exp} [20, 21]
	ν_{harm}	ν_{anh}	ν_{1D}	
$\nu_{\mathrm{BX}}^{A_1'}$ (ν_1)	889	866	887	888
$\nu_{\mathrm{BX}}^{E'}$ (ν_3)	1458	1530 1286	1490 1482	1453
$\delta_{\mathrm{XBX}}^{E'}$ (ν_4)	475	515 326	–	480
$\delta_{\mathrm{XBX}}^{A_2''}$ (ν_2)	683	642	–	691

Let us estimate the frequencies of BF$_3$ molecular symmetric and asymmetric stretching vibrations with neglect of kinematic and force coupling with the bending coordinates. For this, the initially calculated force field was recalculated from mdyn/Å, mdyn·Å/rad^2, and mdyn/rad (for force constants for bond–bond, angle–angle, and bond–angle coupling, respectively) into 10^{-6} cm^{-2} using the coefficients 1.5601, 1.3131, and 1.4313. The calculated equilibrium geometry and force field recalculated in units of cm^{-2} were used to calculate the kinematic-coefficient matrix in pulse mode and the force-constant matrix using the literature [30].

We were interested in the submatrix of the kinematic-coefficient and force-constant matrices of dimension 3 × 3 for coordinates q_1, q_2, and q_3. According to the calculations, they were written:

$$\begin{matrix} 0.1579074 & -0.05031982 & -0.05031877 \\ -0.05031982 & 0.1579074 & -0.05031877 \\ -0.05031877 & -0.05031877 & 0.1579074 \end{matrix} \qquad \begin{matrix} 11.56429 \cdot 10^6 & 1.120427 \cdot 10^6 & 1.112183 \cdot 10^6 \\ 1.120427 \cdot 10^6 & 11.56429 \cdot 10^6 & 1.112183 \cdot 10^6 \\ 1.112183 \cdot 10^6 & 1.112183 \cdot 10^6 & 11.56511 \cdot 10^6 \end{matrix}$$

Let us diagonalize the matrices separately using the fact that the diagonalized matrix is written:

$$\begin{pmatrix} b + 2a & 0 & 0 \\ 0 & b - a & 0 \\ 0 & 0 & b - a \end{pmatrix}, \tag{7}$$

where a are off-diagonal and b, diagonal elements of the starting diagonal matrix.

TABLE 2. Calculated and Experimental Frequencies (ν, cm^{-1}) of BH_3 Vibrations

Mode	B3LYP/cc-pVTZ		B3LYP/cc-pVQZ		B3LYP/acc-pVQZ		B3LYP/acc-pV5Z			
	ν_{harm}	ν_{anh}	ν_{harm}	ν_{anh}	ν_{harm}	ν_{anh}	ν_{harm}	ν_{anh}	ν_{harm} [36]	ν_{exp}
$\nu_{BH}^{A_1'}$ (ν_1)	2565	2503	2564	2507	2564	2507	2564	2510	2567	–
$\nu_{BH}^{E'}$ (ν_3)	2692	2600 2590	2690	2604 2589	2690	2604 2590	2690	2608 2592	2696	2602 [2, 3] 2808 [1]
$\delta_{HBH}^{E'}$ (ν_4)	1205	1186 1201	1206	1186 1203	1206	1187 1203	1206	1194 1209	1223	–1604 [1]
$\delta_{HBH}^{A_2''}$ (ν_2)	1160	1173	1161	1174	1161	1177	1161	1177	1163	1141 [2, 3] 1125 [1]

TABLE 3. Calculated Energies of B–H Totally Symmetric Stretching Vibrations and Transition Frequencies in BH_3

Vibrational quantum number	E_n, cm^{-1}	$\tilde{\nu}_{BH}^{A_1'}$, cm^{-1}	$2\tilde{\nu}_{BH}^{A_1'}$, cm^{-11}	$3\tilde{\nu}_{BH}^{A_1'}$, cm^{-1}	$4\tilde{\nu}_{BH}^{A_1'}$, cm^{-11}
0	1279	–	–	–	–
1	3818	2539	–	–	–
2	6331	–	5052	–	–
3	8820	–	–	7541	–
4	11,283	–	–	–	10,004

Taking into account Matrix (7), we find the following values for the diagonal elements: 0.05727/0.20823 and $13.80514 \cdot 10^6/10.44386 \cdot 10^6$ cm^{-2}, respectively. By multiplying them pairwise after extracting the square root, we obtain the frequencies of the B–F totally symmetric and asymmetric stretching vibrations as 889 and 1474 cm^{-1}. It can be seen that the frequency of the totally symmetric vibration practically did not change whereas that of the asymmetric vibration was in fact greater without coupling with other internal coordinates.

Calculation of BH_3 Vibrational States. It is noteworthy in switching to an examination of BH_3 that the reduced mass according to Eq. (4) in the totally symmetric stretching vibration is equal to the mass of atom X. Because the masses of F and H differ by about 20 times, we were correct to expect that the amplitude of these vibrations should be much greater for BH_3 than for BF_3. The amplitude increase of the molecular vibrations required more complete information about the shape of the PES not only near its minimum but also at rather large distances from it [31–35]. The calculated diagonal anharmonicity constants $\chi_{11}^{BF_3} = -0.799$ cm^{-1} and $\chi_{11}^{BH_3} = -11.644$ cm^{-1} (lower indices correspond to the numbering of normal modes in Tables 1 and 2) were also indicative of greater anharmonicity of B–X stretching vibrations in BH_3 than in BF_3. Table 2 presents frequencies of BH_3 molecular vibrations that were calculated in harmonic and anharmonic approximations using various basis sets in addition to experimental data [1–3] and results of theoretical harmonic calculations of BH_3 vibration frequencies using the CCSD(T)/TZ2P(*f*,*d*) approximation [36].

Table 2 shows that the experimental results [1] raised serious doubts. Moreover, the experimental frequencies of asymmetric stretching and out-of-plane vibrations ($\nu_{BH}^{E'}$ and $\delta_{HBH}^{A_2''}$) agreed well with those calculated in the anharmonic approximation. It is noteworthy that increasing the size of the basis set had little effect on the calculated vibrational frequencies. The 1D-PES for symmetric stretching coordinate q_1^S [Eq. (1)] (Fig. 4) was calculated in the B3LYP/cc-pVTZ approximation.

Table 3 presents the calculated energies of the five deepest-lying A_1'-type vibrational states of BH_3 and the frequencies of fundamental vibration $\nu_{BH}^{A_1'}$ and several of its overtones. By using the known formula [37]

$$\chi_{ii} = \frac{1}{2}\tilde{\nu}_i^{\text{overton}} - \tilde{\nu}_i^{\text{fund}},$$

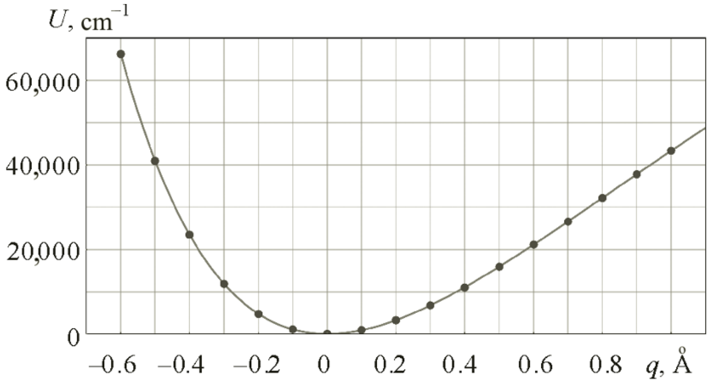

Fig. 4. Calculated potential surface for symmetric vibration $\nu_{\mathrm{BH}}^{A_1'}$.

harmonicity constant χ_{11} for $\nu_{\mathrm{BH}}^{A_1'}$ (–12.54 cm^{-1}) can be found.

The calculated frequency of fundamental vibration $\nu_{\mathrm{BH}}^{A_1'}$ was 2538.54 cm^{-1}. It can be seen that this value was between those obtained in the harmonic (2565 cm^{-1}) and anharmonic (2503 cm^{-1}) approximations. This was analogous to the situation with BF_3. Therefore, there was a basis to assume that the actual B–H totally symmetric stretching frequency in BH_3 was ~2540 cm^{-1}.

Conclusions. The research produced a kinetic energy Hamiltonian in symmetry coordinates. Potential surfaces were calculated using B–H and B–F totally symmetric coordinates and B–F asymmetric coordinates, frequencies of harmonic and anharmonic molecular vibrations of BH_3 and BF_3, and frequencies of B–X totally symmetric stretching vibrations in BH_3 (2538.54 cm^{-1}) and BF_3 (887 cm^{-1}) using a numerical solution of the Schroedinger equation. The calculations agreed well with existing experimental data. Calculations performed using the potential surfaces were preferred over calculations using the standard model for calculating anharmonism effects and simultaneously allowed computation time to be reduced by several orders of magnitude.

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REFERENCES

1. A. Kaldar and R. F. Porter, *J. Am. Chem. Soc.*, **93**, 2140–2145 (1971).
2. K. Kawaguchi, J. E. Butler, C. Yamada, S. H. Bauer, T. Minowa, H. Kanamori, and E. Hirota, *J. Chem. Phys.*, **87**, 2438–2441 (1987).
3. K. Kawaguchi, *J. Chem. Phys.*, **96**, 3411–3415 (1992).
4. D. J. DeFrees and A. D. McLean, *J. Chem. Phys.*, **82**, 333–341 (1985).
5. J. F. Stanton, R. J. Bartlett, and W. N. Lipscomb, *Chem. Phys. Lett.*, **138**, 525–530 (1987).
6. P. Botschwina, in: *Ion and Cluster Ion Spectroscopy and Structure*, J. P. Maier (Ed.), Elsevier, Amsterdam (1989), pp. 76–81.
7. J. M. L. Martin and T. J. Lee, *Chem. Phys. Lett.*, **200**, 502–510 (1992).
8. L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.*, **24**, 242–249 (1956).
9. J. L. Duncan, *J. Mol. Spectrosc.*, **13**, 338–343 (1964).
10. S. N. Dreska and K. N. Rao, *J. Mol. Spectrosc.*, **18**, 404–411 (1965).
11. I. W. Levin and S. Abramowitz, *J. Chem. Phys.*, **43**, 4213–4221 (1965).
12. J. L. Duncan, *J. Mol. Spectrosc.*, **22**, 247–261 (1967).
13. S. G. W. Ginn, C. W. Brown, J. K. Kenney, and J. Overend, *J. Mol. Spectrosc.*, **28**, 509–525 (1968).
14. S. G. W. Ginn, J. K. Kenney, and J. Overend, *J. Chem. Phys.*, **48**, 1571–1578 (1968).
15. C. W. Brown and J. Overend, *Spectrochim. Acta, Part A*, **25**, 1535–1546 (1969).
16. S. G. W. Ginn, D. Johansen, and J. Overend, *J. Mol. Spectrosc.*, **36**, 448–463 (1970).
17. J. Duncan, *J. Mol. Spectrosc.*, **60**, 225–238 (1976).

18. S. Yamamoto, K. Kuchitsu, T. Nakanaga, H. Takeo, C. Matsumura, and M. Takami, *J. Chem. Phys.*, **83**, 1444–1448 (1985).
19. S. Yamamoto, R. Kuwabara, M. Takami, and K. Kuchitsu, *J. Mol. Spectrosc.*, **115**, 333–352 (1986).
20. S. Yamamoto, R. Kuwabara, K. Kuchitsu, T. Nakanaga, H. Takeo, C. Matsumura, and M. Takami, *J. Chem. Phys.*, **84**, 6027–6033 (1986).
21. M. Oldani and A. Bauder, *J. Chem. Phys.*, **86**, 624–628 (1987).
22. http://www.msg.ameslab.gov/GAMESS/GAMESS.html
23. H. Yoshida, K. Takeda, and J. Okamura, *J. Phys. Chem. A*, **106**, 3580–3586 (2002).
24. T. H. Dunning, *J. Chem. Phys.*, **90**, 1007–1023 (1989).
25. J. M. Bouman, *J. Chem. Phys.*, **68**, 608–610 (1978).
26. J. C. Decius, *J. Chem. Phys.*, **16**, 1025–1034 (1948).
27. V. V. Malyshchyts, L. F. Makarenko, G. A. Pitsevich, and A. A. Sokolsky, in: *Abstracts of the International Scientific Conference "Informatization of Education,"* Oct. 27–30, 2010, BSU, Minsk (2010), p. 327.
28. G. Pitsevich, A. Malevich, V. Sablinskas, I. Doroshenko, V. Pogorelov, and V. Balevicius, *J. Spectrosc. Dyn.*, 3:19 (2013).
29. I. M. Mills, in: *Molecular Spectroscopy: Modern Research*, K. N. Rao and C. W. Mathews (eds.), Academic Press, New York (1972), Vol. 1, pp. 115–140.
30. V. V. Sivchik and K. M. Grushetskii, *J. Appl. Spectrosc.*, **19**, 1062–1063 (1975).
31. G. Pitsevich and V. Balevicius, *J. Mol. Struct.*, **1072**, 38–44 (2014).
32. G. Pitsevich, A. Malevich, I. Doroshenko, E. Kozlovskaya, V. Pogorelov, V. Sablinskas, and V. Balevicius, *Spectrochim. Acta, Part A*, **120**, 585–594 (2014).
33. G. Pitsevich, A. Malevich, E. Kozlovskaya, and U. Sapeshko, *J. Spectrosc. Dyn.*, 4:25 (2014).
34. G. Pitsevich and A. Malevich, *Am. J. Chem.*, **2**, 312–321 (2012).
35. P. Golub, I. Doroshenko, and V. Pogorelov, *Phys. Lett. A*, **378**, 1937–1944 (2014).
36. J. M. Galbraith, G. Vacek, and H. F. Schaefer III, *J. Mol. Struct.*, **300**, 281–288 (1993).
37. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules 2*, Van Nostrand Co., New York (1945) [Russian translation, In. Lit., Moscow (1949)].