

---

---

MOLECULAR  
SPECTROSCOPY

---

---

## Observation of IR Absorption Spectra of the Unstable $\text{PbH}_4$ Molecule

V. M. Krivtsun, Yu. A. Kuritsyn, and E. P. Snegirev

*Institute of Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow oblast, 142092 Russia*

Received May 25, 1998

**Abstract**—The IR absorption spectra of the unstable  $\text{PbH}_4$  molecule are studied. The possibility of preparation of  $\text{PbH}_4$  at sufficiently high concentrations ( $\sim 10$  mg/l) in a gaseous phase is demonstrated. The  $\nu_3$  band of  $\text{PbH}_4$  is detected in a gaseous phase by the technique of infrared Fourier spectroscopy. The spectra of  $\text{PbH}_4$  are measured in a low-temperature argon matrix. The basic spectroscopic constants are obtained for the  $\nu_3 = 1-0$  transition, and the position of the  $\nu_4$  band is determined. The results obtained confirm the tetrahedral symmetry of the  $\text{PbH}_4$  molecule.

### INTRODUCTION

The vibration-rotation spectra of molecules of tetrahydrides of the IV group elements such as  $\text{CH}_4$ ,  $\text{GeH}_4$ ,  $\text{SiH}_4$ , and  $\text{SnH}_4$  were extensively studied for many years [1–5]. Molecules of this class serve to test spectroscopic models claiming a detailed description of non-rigid, highly symmetric systems. Recently, tetrahydrides were successfully studied by the method of irreducible tensor operators [2] and using the quasi-classical approach. The vibration-rotation spectra of these molecules were studied by the methods of bifurcation analysis [3, 4], and the so-called critical phenomena observed in their energy spectra were examined [5]. It is of interest to extend the number of tetrahydrides for experimental studies by adding to them the unstable  $\text{PbH}_4$  molecule (plumbane). Because molecular bonds in  $\text{PbH}_4$  are comparatively weak, one can hope to obtain interesting, possibly fundamentally new information on features of the intramolecular dynamics and the interaction between various types of motion in spherical-top molecules.

The  $\text{PbH}_4$  molecule is still poorly examined among a series of hydrides of the IV group elements. The first studies of  $\text{PbH}_4$  [6–8] showed that this molecule is very unstable and it cannot be synthesized by the methods used for the synthesis of  $\text{GeH}_4$  or  $\text{SnH}_4$ . The existence of a compound having the stoichiometry of  $\text{PbH}_4$  was first confirmed only in 1963 by mass spectrometry [9]. A detailed review of studies (more exactly, of the attempts to synthesize and study  $\text{PbH}_4$  before 1975) is presented in [10].

The suggestion to use the method of hydride generation [11, 12] in atomic absorption and emission analysis for the transfer of elements with the subsequent thermal decomposition of hydride stimulated numerous studies on the generation of hydrides of different elements, including lead. Despite the prospects of using  $\text{PbH}_4$  for the transport of lead in atomic analysis, many

authors [12–14] indicated considerable difficulties related to the low yield of lead hydride and its instability. In the recent decade, owing to a great number of papers devoted to the refinement of chemical schemes, the selection of optimum conditions, studies of the kinetics of hydride generation, etc., considerable progress was made towards the synthesis of  $\text{PbH}_4$ . The authors [15–18] managed to transform microgram amounts of lead almost completely to hydride, and the results obtained in [15, 16] show the possibility of preparation of greater amounts of  $\text{PbH}_4$ . However, the aim of all the above papers was the enhancement of the sensitivity of atomic analysis rather than preparation of  $\text{PbH}_4$  in great amounts required for studies of the plumbane molecule itself.

In recent years, a great attention is also being paid to the study of the structure of simplest molecules of heavy elements. Chemical properties of such molecules are substantially determined by relativistic effects, which requires the development of corresponding methods for calculations of the electronic structure of molecules. A number of papers on quantum-mechanical calculations of the equilibrium configuration of hydrides of Pb were performed during two last decades [19–23]. Papers [22, 23] devoted to the influence of relativistic effects on molecular constants of  $\text{PbH}_x$  molecules contain the most comprehensive data, in particular, on  $\text{PbH}_4$ . Note that various calculation models lead to a considerable scatter in the values of basic molecular constants. For example, the values from 1.732 [22] to 1.862 Å [24] were reported for the equilibrium interatomic distance, and from 8.65 [9] to 6.24 eV [22] for the total bond energy of the molecule.

Therefore, experimental studies of the  $\text{PbH}_4$  molecule are of interest both for analytical applications of  $\text{PbH}_4$  and for the development of theoretical models in the field of molecular spectroscopy and quantum chemistry.

PREPARATION OF  $\text{PbH}_4$ 

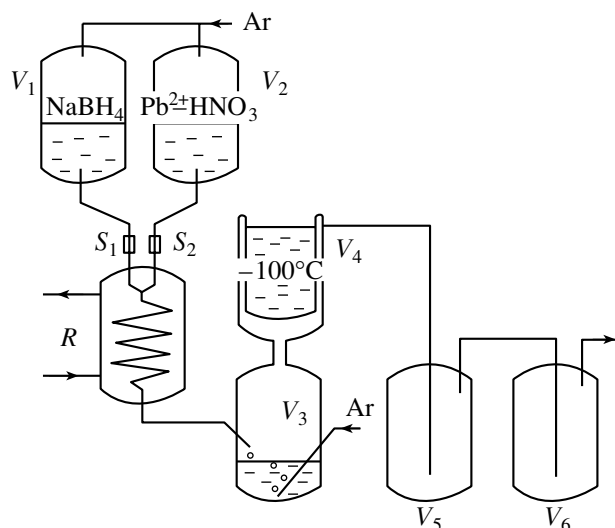
For the hydride generation of  $\text{PbH}_4$ , we used the scheme similar to that described in [15]. Figure 1 shows a scheme of the laboratory setup for synthesis of plumbane. The basic reagents were a 5% solution of  $\text{NaBH}_4$  in 0.1 g-equiv./l  $\text{Ba}(\text{OH})_2$  and a solution of lead nitrate in 0.7 M  $\text{HNO}_3$ . To increase the yield of  $\text{PbH}_4$ , a  $\text{K}_2\text{S}_2\text{O}_8$  oxidizer was added to the nitrous acid solution to saturate the solution at  $10^\circ\text{C}$ . Lead nitrate was added to the solution directly before the performance of the reaction. The reagents were mixed in a reactor  $R$ , which represented five coils of a glass tube with inner diameter of 5 mm. The mixing zone of reagents and a spiral reactor were cooled by means of a water jacket at  $T = 5\text{--}10^\circ\text{C}$ . The reaction products were directed to a gas-liquid separator  $V_3$  from which  $\text{PbH}_4$  was carried out by the  $\text{H}_2$  flow, which was produced in excess during the reaction. Then, gaseous products of the reaction were directed to a flow gas cell through a trap  $V_4$  cooled to  $T = -100^\circ\text{C}$ . The trap served to decrease the amount of water vapors filling a measuring cell.

Special attention was paid to the uniform supply of reagents to the reaction zone and the absence of bubbles and solid particles, because in the case of deviation in the ratio of components (the excess of  $\text{NaBH}_4$ ), reduced elementary lead appears, which causes fast decomposition of  $\text{PbH}_4$ . A contact of reaction products with metals and grease also results in the fast decomposition of  $\text{PbH}_4$ . We determined the amount of prepared  $\text{PbH}_4$  by measuring the mass of Pb carried out by the  $\text{H}_2$  flow from the reactor. For this purpose, we used traps  $V_5$  and  $V_6$  cooled with liquid nitrogen. The traps were evacuated after termination of the reaction and then were heated to room temperature, resulting in a complete decomposition of collected  $\text{PbH}_4$ . The instant of the decomposition could be observed visually by the sharp formation of an opaque black film of amorphous lead on the trap walls, which were transparent at low temperature. The amount of the lead formed was measured by the chemical method and was 3.2 mg per 1 g of  $\text{NaBH}_4$  under optimum conditions of the synthesis.

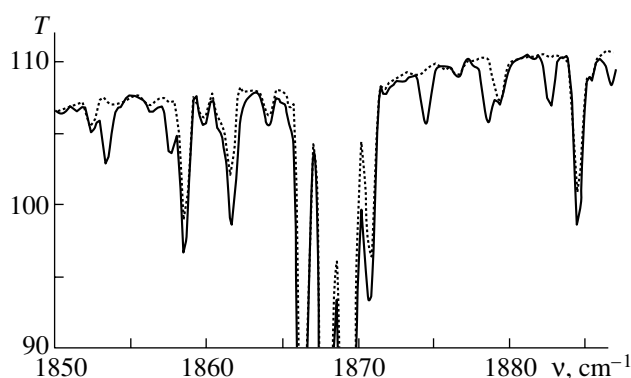
## MEASUREMENTS OF SPECTRA

The spectra were recorded using the setup described above, the only difference being that instead of traps  $V_5$  and  $V_6$  a flow gas cell of 1.0 m with inner diameter of 50 mm was installed. The volume of reagents used was  $100\text{ cm}^3$  each, and the supply rate of reagents was  $\approx 1\text{ cm}^3/\text{s}$ . Prior to the  $\text{PbH}_4$  generation, the whole system, including a gas cell, was pumped out and filled with argon up to atmospheric pressure.

Absorption spectra were recorded with a Fourier spectrometer with a resolution of  $0.1\text{ cm}^{-1}$ . The spectrometer is based on a classical Michelson interferometer with plane mirrors. The interferometer is equipped with a system of dynamic adjustment of mirrors. Interferograms were accumulated upon continu-



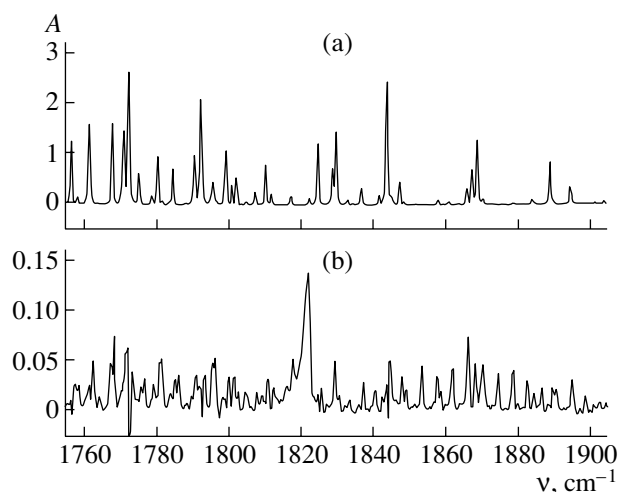
**Fig. 1.** Scheme of the setup for hydride-generation of plumbane.  $V_1$  and  $V_2$  are burets with reagents,  $S_1$  and  $S_2$  are calibrated leaks,  $R$  is a water-cooled reactor,  $V_3$  is a gas-liquid separator,  $V_4$  is a trap cooled by a mixture of liquid nitrogen and benzene to  $-100^\circ\text{C}$ , and  $V_5$  and  $V_6$  are traps cooled by liquid nitrogen.



**Fig. 2.** Transmission spectrum in the  $1850\text{--}1885\text{-cm}^{-1}$  region (the  $R$ -branch of the  $\nu_3$  band of the  $\text{PbH}_4$  molecule). The solid curve is the spectrum recorded during hydride-generation of plumbane; the dashed curve is the spectrum recorded  $\approx 2$  min after termination of the reaction.

ous scanning optical path difference. A platinum ceramic radiator built in the spectrometer was used as a radiation source. The radiation emerged from the interferometer through a window in its body and, after passage through a gas cell, was focused on a pyroelectric detector with the help of a  $\text{KBr}$  prism with the focal distance  $F = 100\text{ mm}$ .

The control of the spectrometer, the accumulation of interferograms and the reconstruction of spectra were performed with a 486 DX4 PC. The scan rate of the optical path difference of  $3.15\text{ mm/s}$  and resolutions of  $0.62$  and  $0.26\text{ cm}^{-1}$  were chosen to match the Fourier spectrum with the frequency band of the photodetector by retaining the maximum signal-to-noise ratio in the



**Fig. 3.** Spectrum in the region of the  $Q$ -branch of the  $\nu_3$  band of plumbane: (a) absorption spectrum of water vapors, (b) absorption spectrum of  $\text{PbH}_4$  (absorption by stable reaction products is subtracted from the total spectrum).

spectrum. In addition, we were restricted by the duration of continuous generation of  $\text{PbH}_4$ , which did not exceed 120 s. For the chosen scan rate of 3.15 mm/s, the accumulation time of a two-sided interferogram was 18 and 9 s in the case of the use of parabolic apodization and spectral resolution of 0.26 and 0.52  $\text{cm}^{-1}$ , respectively. Because the intensity of absorption lines of water and  $\text{CO}_2$  can rapidly change during the displacement of Ar from a gas cell by reaction products, we measured spectra 20 s after the reaction onset. One can

easily estimate from the consumption of  $\text{NaBH}_4$  that for the rate of the hydrogen formation  $\sim 85 \text{ cm}^3/\text{s}$ , this time is sufficient for the filling of more than 60% of the cell volume. We managed to perform 10–11 accumulations of the interferogram with a resolution of 0.52  $\text{cm}^{-1}$  and 4–5 accumulation with a resolution of 0.26  $\text{cm}^{-1}$ . After completion of the reaction, an outlet valve of the gas cell was closed, and two reference spectra were successively recorded, each of them with a double number of accumulations as compared to that used for the working spectrum. This method allowed us to eliminate the interfering lines of water vapors and to separate, among the emerging lines related to the reaction products, the lines belonging to unstable compounds.

We performed five recordings of the spectrum: two with a resolution of 0.52  $\text{cm}^{-1}$ , two with a resolution of 0.26  $\text{cm}^{-1}$ , and one control spectrum was recorded under the same conditions, but  $\text{Pb}^{2+}$  was not charged into the reactor. The  $\nu_3$  band with the  $Q$ -branch at the frequency  $\nu_0 \approx 1822 \text{ cm}^{-1}$  was easily identified from comparison of the characteristic form of the  $Q$ - and  $R$ -branches in the spectra. Although the  $P$ -branch was located in the region of strong absorption by water vapors, it was discernible. These branches were always present in all four spectra upon generation of  $\text{PbH}_4$ , but they were not found in a control experiment and completely disappeared in the first spectrum recorded after  $\text{PbH}_4$  ceased to form. Moreover, according to [25], neither of known spherical-top molecules or linear molecules with the rotational constant close to 2.2  $\text{cm}^{-1}$  has fundamental transitions in the region  $1822 \pm 50 \text{ cm}^{-1}$ . Recall that in [24], the position of the  $\nu_3$   $\text{PbH}_4$  band of  $\text{PbH}_4$  was predicted at 1750  $\text{cm}^{-1}$ , which is lower than the

**Table 1.** Transitions in the  $\nu_3$  band of the  $\text{PbH}_4$  molecule determined from experiments

Transition assignment	Experiment, $\text{cm}^{-1}$	Weight	Transition assignment	Experiment, $\text{cm}^{-1}$	Weight
			R0	1827.12	0.01
			R1	1831.95	0.001
P2	1814.3	0.0001	R2	1835.96	0.1
P3	1809.11	0.01	R3	1840.32	1.0
P4	1804.57	0.03	R4	1844.68	0.01
P5	1800.00	0.01	R5	1849.04	0.30
P6	1795.30	0.03	R6	1853.33	1.0
P7	1790.66	0.001	R7	1857.62	0.30
P8	1786.05	0.10	R8	1861.87	1.0
P9	1781.29	0.03	R9	1866.10	1.0
P10	1776.64	0.10	R10	1870.26	0.30
P11	1772.00	0.0001	R11	1874.46	1.0
P12	1767.26	0.0003	R12	1878.54	1.0
P13	1762.30	0.0001	R13	1882.63	1.0
			R14	1886.68	1.0
Q1	1822.90	0.30	R15	1890.60	0.130
			R16	1895.03	0.01
			R17	1898.63	1.0
			R18	1902.56	0.1

value we found, whereas calculations [22] yielded the overestimated value of the frequency of stretching vibrations.

Absorption at the maximum of the  $Q$ -branch was  $\approx 12\%$ , which represented 20–25% of the value estimated from measurements of the yield of  $\text{PbH}_4$  by assuming that the band intensity is close to that for the  $\text{SnH}_4$  molecule. This discrepancy can be explained by the fact that  $\text{PbH}_4$  does not fill the whole volume of the gas cell after its decomposition. Figure 2 shows the experimental spectrum in the region of the  $R$ -branch of the  $\nu_3$  band. The main obstacle to the measurement of the spectrum proved to be not a low concentration of  $\text{PbH}_4$  but a great number of strong absorption lines of water vapors, which we failed to separate completely from the reaction products in the rapid flow. The mathematical separation of the spectra based on the recalculation of absorption between two close concentrations using the Beer law also was inefficient, first, due to the low spectral resolution, which did not allow us to record a true absorption band and, second, because of nonstationary absorption during recording of the spectrum of  $\text{PbH}_4$ . In addition, we found from analysis of the spectrum in the control experiment without lead that the intensity of some lines of water vapors changed with temperature.

Figure 3b shows a part of the spectrum of  $\text{PbH}_4$  after partial elimination of lines of  $\text{H}_2\text{O}$ . Absorption of  $\text{PbH}_4$  was identified from all the four spectra recorded, in which only repeated lines were selected which were absent in the control experiment. Note that for  $J \geq 10$ , the spectrum of the  $R$ -branch becomes complicated: additional groups of lines appear between regular mul-

tiplets. Although these lines belong undoubtedly to  $\text{PbH}_4$ , we did not consider them. The identified transitions are listed in Table 1. In the column "weight", the weight factor is presented which characterizes the reliability of the data. In most cases, it was estimated in accordance with the distance between lines of  $\text{PbH}_4$  and  $\text{H}_2\text{O}$ .

The accuracy of measuring of the wave numbers  $\nu_{\text{obs}}$  was determined from frequencies of 15 well-isolated lines of  $\text{H}_2\text{O}$  which were compared with the values of  $\nu_{\text{tr}}$  reported in [26]. For the spectra recorded with a resolution of  $0.26 \text{ cm}^{-1}$ , the systematic deviation was  $\Delta\nu = \langle \nu_{\text{obs}} - \nu_{\text{tr}} \rangle = -0.02 \text{ cm}^{-1}$  and the root-mean-square deviation  $\langle (\nu_{\text{obs}} - \nu_{\text{tr}})^2 \rangle^{1/2} = 0.02 \text{ cm}^{-1}$ , and for the spectra recorded with a resolution of  $0.52 \text{ cm}^{-1}$ , those quantities were  $-0.03$  and  $0.02 \text{ cm}^{-1}$ , respectively.

We used the data presented in Table 1 to fit basic spectroscopic constants of the  $\text{PbH}_4$  molecule in the simplest model of a rigid spherical top with the first-order Coriolis splitting for the triply degenerate  $\nu_3 = 1$  level and the non-degenerate ground state. The rotational part of the energy was represented in the form [27]

$$F_3^{(+)}(J) = B_3 J(J+1) + 2B_3 \xi_3(J+1),$$

$$F_3^{(0)}(J) = B_3 J(J+1),$$

$$F_3^{(-)}(J) = B_3 J(J+1) - 2B_3 \xi_3 J,$$

$$F_0(J) = B_0 J(J+1).$$

Here, subscripts 0 and 3 denote the unsplit ground state and the  $\nu_3 = 1$  state, respectively.

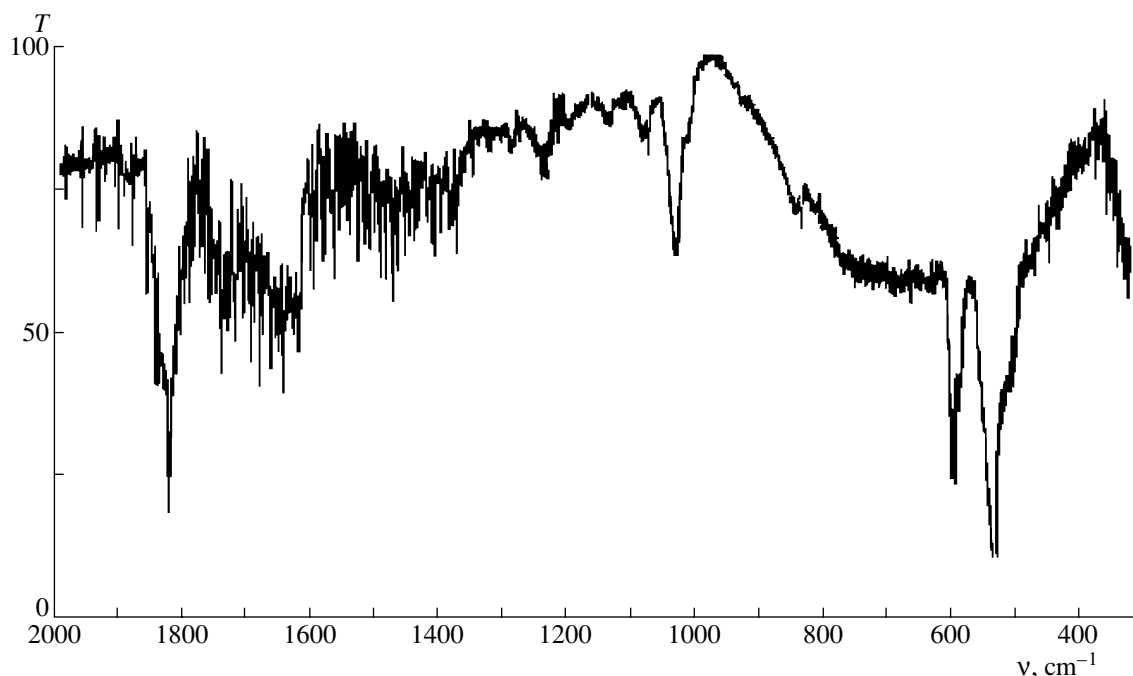


Fig. 4. Transmission spectrum of  $\text{PbH}_4$  in an argon matrix at  $\approx 10 \text{ K}$ .

**Table 2.** Values of spectroscopic constants for the  $\nu_3$  band of the  $\text{PbH}_4$  molecule

$\nu_3 = 1822.956 \text{ cm}^{-1}$	$B_0 = 2.0844 \text{ cm}^{-1}$
$\xi_3 = -0.0828 \text{ cm}^{-1}$	$B_3 = 2.0694 \text{ cm}^{-1}$

Results of calculations for the  $\nu_3$  band of the  $\text{PbH}_4$  molecule

Transition assignment	$\nu_{\text{exp}} - \nu_{\text{calc}}, \text{ cm}^{-1}$	Calculation, $\text{ cm}^{-1}$	Transition assignment	$\nu_{\text{exp}} - \nu_{\text{calc}}, \text{ cm}^{-1}$	Calculation, $\text{ cm}^{-1}$
			R0	+0.024	1827.1
			R1	+0.406	1831.55
P2	+0.397	1813.95	R2	-0.009	1835.97
P3	-0.220	1809.33	R3	-0.040	1840.36
P4	-0.158	1804.73	R4	-0.041	1844.72
P5	-0.096	1800.1	R5	-0.012	1849.05
P6	-0.133	1795.43	R6	-0.023	1853.35
P7	-0.081	1790.74	R7	-0.004	1857.62
P8	+0.032	1786.02	R8	+0.006	1861.86
P9	+0.026	1781.26	R9	+0.025	1866.07
P10	+0.159	1776.48	R10	+0.005	1870.25
P11	+0.332	1771.67	R11	+0.055	1874.4
P12	+0.435	1766.82	R12	+0.015	1878.52
P13	+0.349	1761.95	R13	+0.016	1882.61
			R14	+0.006	1886.67
Q1	-0.028	1822.93	R15	-0.103	1890.7
			R16	+0.327	1894.7
			R17	-0.042	1898.67
			R18	-0.051	1902.61

The results of calculations of  $\nu_3$ ,  $B_0$ ,  $B_3$ , and  $\xi_3$  are presented in Table 2. The accuracy of measuring  $\xi_3$  is poor, as is expected for calculations only from the  $\nu_3$  band, the data for transitions in the *P*-band being unreliable. A set of combinations  $B_3 - B_0$ ,  $B_3(1 - \xi_3)$ ,  $\nu_3 - Q(1)$ ,  $B_0$  can be calculated more accurately, however, these quantities also can change substantially when higher terms in the energy of rotational multiplets and the interaction with the  $\nu_1 = 1$  state, whose energy is unknown at present, are taken into account.

We failed to determine the position of another allowed  $\nu_4$  band from Fourier spectra because of the strong absorption  $\nu_2$  band of  $\text{CO}_2$  and the inadequate signal-to-noise ratio in the region from 500 to 700  $\text{ cm}^{-1}$ .

The position of the  $\nu_4$  band was determined from low-temperature ( $\approx 10 \text{ K}$ ) spectra of  $\text{PbH}_4$  in an argon matrix recorded earlier (Fig. 4).<sup>1</sup> The frequency shift of the  $\nu_3$  stretching vibration in an argon matrix was  $\approx -10 \pm 6 \text{ cm}^{-1}$ . We found the low-frequency band at 602  $\text{ cm}^{-1}$  from the intensity correlations under different conditions of generation of  $\text{PbH}_4$  and interpreted it as the  $\nu_4$  band of the  $\text{PbH}_4$  molecule. Earlier [24], the value  $\nu_4 = 574 \pm 19 \text{ cm}^{-1}$  was predicted. It is unlikely

that the difference in 30  $\text{ cm}^{-1}$  can be explained by the frequency shift in a matrix, which does not exceed several  $\text{ cm}^{-1}$  for tetrahydrides. Nevertheless, the existence of the low-frequency mode additionally confirms the tetrahedral symmetry of  $\text{PbH}_4$ .

## DISCUSSION AND CONCLUSIONS

This work represents a preliminary stage of high-resolution studies of spectra of the  $\text{PbH}_4$  molecule using a spectrometer with tunable semiconductor lasers. Our experiments showed that  $\text{PbH}_4$  could be quite easily obtained in a gas phase in amounts sufficient for spectroscopic studies of this molecule in the IR spectral region.

Contrary to many statements about the extreme instability of  $\text{PbH}_4$ , the lifetime of these molecules in our system in the hydrogen atmosphere at the atmospheric pressure was about 10 s. Although we did not study mechanisms of the decomposition of  $\text{PbH}_4$  in this paper, some conclusions can be made here. The efficiency of the reaction  $\text{PbH}_4 + \text{PbH}_4 \rightarrow \text{products}$  does not exceed  $3 \times 10^{-3}$  per gas-kinetic collision. The sharp acceleration of the decomposition of  $\text{PbH}_4$  as its concentration increases is caused by the appearance of free lead, which enhances the decomposition process. It is possible that most of  $\text{PbH}_4$  is decomposed due to reac-

<sup>1</sup> Spectroscopic studies of  $\text{PbH}_4$  in matrices were performed in collaboration with researchers from Moscow State University. However, we did not publish these results earlier because they were not reliably confirmed.

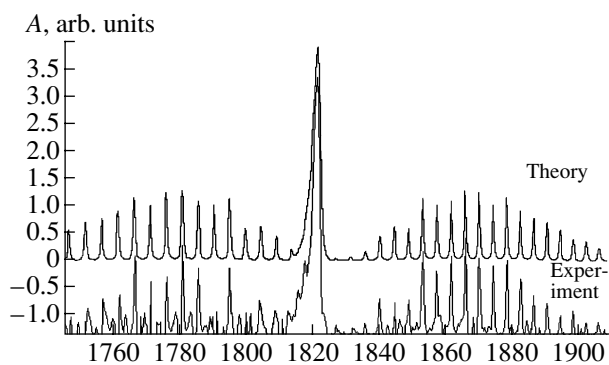


Fig. 5. Calculated and experimental absorption spectra of plumbane in the region of the  $\nu_3$  band between 1740 and 1920  $\text{cm}^{-1}$ .

tion with a wall, because we found great amounts of metal lead at narrowing sites of the flow.

The simulation of the  $\nu_3$  band revealed good agreement between measured and calculated intensities for the  $\text{PbH}_4$  molecule, taking into account nuclear statistical weights. The calculated absorption band is shown in Fig. 5. This agreement conclusively proves the tetrahedral symmetry of this molecule.

The measured frequencies of fundamental bands  $\nu_1$  and  $\nu_4$  are close to theoretical quantum-mechanical values [22, 23]. The frequencies of transitions in the  $R$ - and  $P$ -branches and the position of the  $Q$ -branch of the  $\nu_3$  band measured by us show that the  $\nu_3$  band can be studied with high resolution with the help of diode lasers. Note that the use of a Fourier spectrometer for this purpose is inefficient, because the time required for the detection of the spectrum with a resolution of  $\sim 10^{-3} \text{ cm}^{-1}$  would be at least several tens of minutes, which is unacceptable since the cell and supply tubes become covered with a lead deposit after 10–15 min of the operation time.

Based on the spectroscopic constants presented in Table 2, we estimated the equilibrium distance  $r_e(\text{Pb-H})$  in the  $\text{PbH}_4$  molecule as  $1.73 \pm 0.01 \text{ \AA}$ . This value is close to values 1.732–1.739  $\text{ \AA}$  obtained from calculations of pseudopotentials, taking into account relativistic corrections [22, 23]. However, because of a strong correlation dependence of  $B_0$  on  $\xi_3$ , which we determined only approximately, the value of  $r_e$  should be refined.

#### ACKNOWLEDGMENTS

The authors thank Microtech company for placing a Fourier spectrometer at our disposal for these measurements. The work was supported by the International Science Foundation (grant no. MU 4300) and the Russian Foundation for Basic Research (project no. 95-02-04466a).

#### REFERENCES

1. Champion, J.-P. and Pierre, G., *J. Mol. Spectrosc.*, 1980, vol. 79, no. 2, p. 255.

2. Zhilinskii, B.I., *Metod neprivodimykh tenzornykh operatorov v molekulyarnoi spektroskopii* (Method of Irreducible Tensor Operators in Molecular Spectroscopy), Moscow: Mosk. Gos. Univ., 1981.
3. Zhilinskii, B.I. and Pavlichenkov, I.M., *Dokl. Akad. Nauk SSSR*, 1986, vol. 288, no. 2, p. 355.
4. Krivtsun, V.M., Sadovskii, D.A., and Snegirev, E.P., *Opt. Spektrosk.*, 1991, vol. 70, no. 5, pp. 1007–1010.
5. Krivtsun, V.M., Sadovskii, D.A., and Zhilinskii, B.I., *J. Mol. Spectrosc.*, 1990, vol. 139, no. 1, p. 126.
6. Paneth, F., *Z. Electrochem.*, 1920, vol. 26, p. 452.
7. Paneth, F. and Furth, K., *Ber. Deut. Chem. Ges.*, 1919, vol. 52, p. 2020.
8. Paneth, F. and Rabinowitsch, E., *Ber. Deut. Chem. Ges.*, 1924, vol. 57, p. 1877.
9. Saalfeld, F.E. and Svec, H.J., *Inorg. Chem.*, 1963, vol. 2, p. 46.
10. Porritt, C.-J., *Chemistry and Industry*, 1975, 3 May, p. 398.
11. Holak, H., *Anal. Chem.*, 1969, vol. 41, p. 1712.
12. Thomson, K.C. and Thomerson, D.R., *Analyst* (London), 1974, vol. 99, p. 595.
13. Chapman, J.F. and Lale, L.S., *Anal. Chim. Acta*, 1979, vol. 111, p. 137.
14. Godden, R.D. and Thomerson, D.R., *Analyst* (London), 1980, vol. 105, p. 1137.
15. Jin, K. and Taga, M., *Anal. Chim. Acta*, 1982, vol. 143, p. 229.
16. Aznarez, J., Palacios, F., Vidal, J.C., and Galban, J., *Analyst* (London), 1984, vol. 109, p. 713.
17. Bonilla, M., Rodrigues, L., and Camara, C., *J. Anal. At. Spectrom.*, 1987, vol. 2, no. 2, p. 157.
18. Fernandes de la Campa, M.R., Segovia Garcia, E., Valdes Hevia y Tamprano, M.C., Aizpun Fernandez, B., Marchante Gayon, J.M., and Sanz-Madel, A., *Spectrochim. Acta, Part B*, 1995, vol. 50, nos. 4–7, pp. 377.
19. Hensen, K., Achatz, M., Muller, R., and Trobs, U., *Theor. Chim. Acta* (Berlin), 1974, vol. 34, p. 327.
20. Desclaux, J.P. and Pyykko, P., *Chem. Phys. Lett.*, 1974, vol. 29, no. 4, p. 534.
21. Dyal, K.J., Taylor, P.R., Faegri, K., Jr., and Partridge, H., *J. Chem. Phys.*, 1991, vol. 95, no. 4, p. 2583.
22. Schwerdtfeger, P., Silberbach, H., and Miehlich, B., *J. Chem. Phys.*, 1989, vol. 90, no. 2, p. 762.
23. Wang, S.G. and Schwarz, W.H.E., *J. Mol. Struct.*, 1995, vol. 338, p. 347.
24. Yushin, A.S. and Mikheev, V.S., *Meeting of the Editorial Board of Zh. Fiz. Khim.*, Available from VINITI, 1974, Moscow, no. 6987-73.
25. *Molekulyarnye postoyannye neorganicheskikh soedinenii* (Molecular Constants of Inorganic Compounds), Krasnov, K.S., Ed., Leningrad: Khimiya, 1979.
26. Guelachvli, G. and Rao, K.N., *Handbook of Infrared Standards*, Orlando, 1983.
27. Herzberg, G. *Molecular Spectra and Molecular Structure*, New York: Van Nostrand, 1945, vol. 2. Translated under the title *Kolebatel'nye i vrashchatel'nye spektry mnogoatomnykh molekul*, Moscow: Inostrannaya Literatura, 1947.

Translated by M. Sapozhnikov