

# Complexes with inorganic hydrides (NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>)

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The optimal structures and harmonic vibrational frequencies of water complexes with NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub> have been determined by the Restricted Hartree–Fock (RHF) and second order Möller–Plesset perturbation theory (MP2) with augmented correlation consistent double zeta basis set for NH<sub>3</sub>–H<sub>2</sub>O, PH<sub>3</sub>–H<sub>2</sub>O complexes and 6-31++G(d, p) basis set for AsH<sub>3</sub>–H<sub>2</sub>O. At the MP2 level, this basis set yields very accurate results for the structure, dipole moment, and harmonic vibrational frequencies of water monomer. Analysis of the structural trends revealed that the separation between the neighboring oxygen atom and the X (N, P, As) atom increases in the row from N to As. The harmonic vibrational frequencies corresponding to OH<sub>b</sub> (“bridge” hydrogen) stretches show large red shift by 224 cm<sup>-1</sup> for the NH<sub>3</sub>–H<sub>2</sub>O complex, but for PH<sub>3</sub>–H<sub>2</sub>O and AsH<sub>3</sub>–H<sub>2</sub>O these shifts are about 20 cm<sup>-1</sup>. The intensities corresponding to the OH<sub>b</sub> stretches increase several orders of magnitude as a result of H-bonding. The intensity patterns are analyzed by means of electronic density redistribution, which reveals that intensification of the proton donor stretch is chiefly due to the increasing charge flux associated with H-bond formation.

## Introduction

Ammonia is of greatest interest for ordinary atmospheric chemistry. Such hydrides as PH<sub>3</sub> and AsH<sub>3</sub> may present in trace amounts in the atmosphere. The structure of the  $\bar{1}_2\bar{1} \dots \text{NH}_3$  was studied for the first time by the method of rotational spectroscopy in Refs. 1 and 2. The spectra in the microwave and far infrared regions (36–86 and 520–800 GHz, respectively) of the water–ammonia complex were studied in Ref. 3. Almost free rotation of the NH<sub>3</sub> molecule in the complex with the barrier of  $(10.5 \pm 5.0) \text{ cm}^{-1}$  were observed experimentally, as well as the  $\bar{1}_2\bar{1}$  tunneling effect leading to exchange of two protons in the water molecule with the barrier of 700 cm<sup>-1</sup>. Fine spectral effects in the region of NH<sub>3</sub> umbrella mode at 1021 cm<sup>-1</sup> were studied with a specialized IR spectrometer in Ref. 4. The observed set of vibrationally averaged rotational constants of the complex is better described by the presence of the “bent” intermolecular hydrogen bond in the complex (deviation of 10° from the linear configuration).

The  $\bar{1}_2\bar{1} \dots \text{NH}_3$  complex in low-temperature matrices was studied by the IR spectroscopic method in the region of 4000–300 (Ref. 5) and 4000–10 cm<sup>-1</sup> (Ref. 6). The longwave shift  $\Delta\nu_{\bar{1}\bar{1}}$  of the  $\nu_1$  and  $\nu_2$  water bands in the  $\bar{1}_2\bar{1} \dots \text{NH}_3$  complex as compared to the corresponding values of the free water molecule almost twice exceeds that for the water dimer.<sup>7</sup> Based on the almost linear dependence between enthalpy of complex formation  $\Delta\bar{f}_f$  and the value of  $\Delta\nu_{\bar{1}\bar{1}}$  for the

series of proton acceptors at the same donor, we can assume that  $\Delta\bar{f}_f$  for this complex will be roughly twice as large as that for the water dimer, that is,  $(-5.2 \pm 1.5) \text{ kcal}\cdot\text{mol}^{-1}$  (Ref. 8). In Ref. 6 the principal attention was paid to analysis of low-frequency bands of intermolecular vibrations in the complex, and the bands nearby 19.5 cm<sup>-1</sup> was assigned to the torsion vibration of the linearly (N... $\bar{1}$ – $\bar{1}$ ) H-bonded water molecule around the symmetry axis of the complex, while the ammonia molecule remains fixed relative to the matrix. Stockman et al.<sup>3</sup> have assigned this band, taking into account the results of microwave and IR spectroscopic studies of this complex in the gas phase, to the rotation-torsion transitions of the water molecule lying between 20 and 22 cm<sup>-1</sup>. In Refs. 9, 10, and 12–16 the potential surface of the  $\bar{1}_2\bar{1} \dots \text{NH}_3$  complex and its vibrational spectrum were studied by quantum-chemistry methods.

The complexes of hydrides of elements belonging to the VA group of the low-lying periods (PH<sub>3</sub>, AsH<sub>3</sub>) with water in the gas phase are still almost unstudied. In Ref. 11 the comparative calculation of the structure and energy of the  $\bar{1}_2\bar{1} \dots \text{NH}_3$  and  $\bar{1}_2\bar{1} \dots \text{PH}_3$  complexes was performed (Table 1, where  $R = |\text{O}\dots\text{N}|$ ;  $r = |\text{O}-\text{H}|$ ;  $\theta = \angle\text{H}-\text{O}\dots\text{X}$ ;  $\Delta E$  is the bond energy with allowance for the electronic correlation calculated by the MP2 method;  $\Delta H^{\bar{f}}$  is the enthalpy of the formation process). The strength of the complex with participation of phosphine is several times lower than that of the complex with participation of ammonia.

Table 1. Geometry and energy parameters of complexes

Complex	Basis set	$R, \text{ \AA}$	$r, \text{ \AA}$	$\theta, \text{ deg}$	$\Delta\bar{A}, \text{ MP2, kcal/mol}$	$\Delta H^{\bar{f}}, \text{ kcal/mol}$	Ref.
H <sub>2</sub> O...NH <sub>3</sub>	6-31G++(2d, 2p)	3.039	0.955	2.3	-6.6	-4.7	17
	6-31G**+VP <sup>s</sup> (2d)	3.096	0.930	4.6	-6.48	-4.16	18
H <sub>2</sub> O...PH <sub>3</sub>	6-31G++(2d, 2p)	3.918	0.949	3.0	-2.2	-0.8	19

In this paper we theoretically investigate the complexes of  $\text{NH}_3$  and  $\text{PH}_3$  in the augmented correlation consistent double zeta basis set aug-cc-pVDZ, calculate the structure and energy characteristics of the  $\text{AsH}_3$  complex in the 6-31G(d, p) and 6-31++G(d, p) basis sets, determine the vibrational frequencies of the complexes considered, and analyze the main spectroscopic manifestations at H-bonding. Calculations are performed using Gaussian-98, Restricted Hartree–Fock (RHF) and second order Möller–Plesset perturbation theory (MP2) (Ref. 24).

## Theory

### Vibrational analysis in *ab initio* calculations

#### Mass-weighted Hessian and diagonalization

Let us begin our study from the determination of the Hessian matrix  $\mathbf{f}_{\text{CART}}$ , which includes second partial derivatives of the potential  $V$  with respect to displacement of atoms in the Cartesian coordinates (CART):

$$f_{\text{CART},ij} = \left( \frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right)_0. \quad (1)$$

It is the  $3N \times 3N$  matrix ( $N$  is the number of atoms), where  $\xi_1, \xi_2, \xi_3, \dots, \xi_{3N}$  are used for displacements in the Cartesian coordinates,  $\Delta x_1, \Delta y_1, \Delta z_1, \dots, \Delta z_N$ . The designation  $( )_0$  refers to the fact that the derivatives are taken at the equilibrium positions of the atoms, and that the first derivatives are zero. Then these force constants are converted to the mass-weighted Cartesian coordinates:

$$f_{\text{MWC},ij} = \frac{f_{\text{CART},ij}}{\sqrt{m_i m_j}} = \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0, \quad (2)$$

where  $q_1 = \sqrt{m_1} \xi_1 = \sqrt{m_1} \Delta x_1, q_2 = \sqrt{m_1} \xi_2 = \sqrt{m_1} \Delta y_1$ , and so on are the mass-weighted Cartesian coordinates. The matrix  $\mathbf{f}_{\text{MWC}}$  is diagonalized, yielding a set of  $3N$  eigenvectors and  $3N$  eigenvalues. The eigenvectors, which are the normal modes, are discarded; they will be calculated again after the rotation and translation modes are separated. The roots of the eigenvalues are the fundamental frequencies of the molecule. They are converted to  $\text{cm}^{-1}$ . In general, the frequencies for rotation and translation modes should be close to zero. If there is a transition state or a higher order saddle point, then there will appear some negative frequencies.

#### Determination of the principal axes of inertia

The center of mass ( $\mathbf{R}_{\text{COM}}$ ) is found in the usual way:

$$\mathbf{R}_{\text{COM}} = \sum_{\alpha} m_{\alpha} \mathbf{r}_{\alpha} / \sum_{\alpha} m_{\alpha}, \quad (3)$$

where the sums are over the atoms  $\alpha$ . The origin is then shifted to the center of mass  $\mathbf{r}_{\text{COM}\alpha} = \mathbf{r}_{\alpha} - \mathbf{R}_{\text{COM}}$ . Next we have to calculate the moments of inertia (diagonal elements) and the products of inertia (off-diagonal elements) of the moment of inertia tensor ( $\mathbf{I}$ ):

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} = \begin{pmatrix} \sum_{\alpha} m_{\alpha} (y_{\alpha}^2 + z_{\alpha}^2) & -\sum_{\alpha} m_{\alpha} (x_{\alpha} y_{\alpha}) & -\sum_{\alpha} m_{\alpha} (x_{\alpha} z_{\alpha}) \\ -\sum_{\alpha} m_{\alpha} (y_{\alpha} x_{\alpha}) & \sum_{\alpha} m_{\alpha} (x_{\alpha}^2 + z_{\alpha}^2) & -\sum_{\alpha} m_{\alpha} (x_{\alpha} z_{\alpha}) \\ -\sum_{\alpha} m_{\alpha} (z_{\alpha} x_{\alpha}) & -\sum_{\alpha} m_{\alpha} (z_{\alpha} y_{\alpha}) & \sum_{\alpha} m_{\alpha} (x_{\alpha}^2 + y_{\alpha}^2) \end{pmatrix}. \quad (4)$$

This symmetric matrix is diagonalized, yielding the principal moments (the eigenvalues  $\mathbf{I}'$ ) and a  $3 \times 3$  matrix ( $\mathbf{\tilde{O}}$ ) which is made up of the normalized eigenvectors of  $\mathbf{I}$ . The eigenvectors of the moment of inertia tensor are used to generate the vectors corresponding to translation and infinitesimal rotation of the molecule.

#### Separation of rotation and translation motion

Consider generation of the transformation of  $\mathbf{D}$  from the mass-weighted Cartesian coordinates to a set of  $3N$  coordinates, where rotation and translation of the molecule are separated, leaving  $3N - 6$  or  $3N - 5$  modes for vibrational analysis.

The three vectors ( $\mathbf{D}_1, \mathbf{D}_2, \mathbf{D}_3$ ) of length  $3N$  corresponding to translation are trivial to generate in the Cartesian coordinates (Sayvetz relationship). They are just  $\sqrt{m_i}$  times the corresponding coordinate axis. For example, for  $m_{\text{H}} = 1$  and  $m_{\text{O}} = 16$  the translational vectors are

$$\mathbf{D}_1 = (1, 0, 0, 4, 0, 0, 1, 0, 0)^{\text{T}},$$

$$\mathbf{D}_2 = (0, 1, 0, 0, 4, 0, 0, 1, 0)^{\text{T}},$$

$$\mathbf{D}_3 = (0, 0, 1, 0, 0, 4, 0, 0, 1)^{\text{T}}.$$

The vectors corresponding to rotational motion of atoms in the Cartesian coordinates can be written as

$$\begin{aligned} D_{4j,i} &= [(P_y)_i X_{j,3} - (P_z)_i X_{j,2}] / (m_i)^{1/2}, \\ D_{5j,i} &= [(P_z)_i X_{j,1} - (P_x)_i X_{j,3}] / (m_i)^{1/2}, \\ D_{6j,i} &= [(P_x)_i X_{j,2} - (P_y)_i X_{j,1}] / (m_i)^{1/2}, \end{aligned} \quad (5)$$

where  $j = x, y, z$ ,  $i$  is over all atoms, and  $P$  is the dot product of  $\mathbf{R}$  (the coordinates of the atoms with respect to the center of mass) and the corresponding row of  $\mathbf{X}$ . The next step is to normalize these vectors using the reciprocal square root of the scalar product.

A Schmidt orthogonalization is used to generate  $N_{\text{vib}} = 3N - 6$  (or  $3N - 5$ ) remaining vectors, which are orthogonal to the five or six rotational and translational vectors. The result is the transformation matrix  $\mathbf{D}$ , which transforms from the mass-weighted Cartesian coordinates  $\mathbf{q}$  to the internal coordinates  $\mathbf{S} = \mathbf{D} \mathbf{q}$ , where rotation and translation have been separated.

### Hessian transformation to internal coordinates and diagonalization

When transforming the Hessian  $\mathbf{f}_{\text{MWC}}$  to the new internal coordinates (INT), only the  $N_{\text{vib}}$  coordinates corresponding to internal coordinates will be diagonalized, although the full  $3N$  coordinates are used to transform the Hessian. The transformation is straightforward:

$$\mathbf{f}_{\text{INT}} = \mathbf{D}^\dagger \mathbf{f}_{\text{MWC}} \mathbf{D}. \quad (6)$$

The  $N_{\text{vib}} \times N_{\text{vib}}$  submatrix of  $\mathbf{f}_{\text{INT}}$ , which represents the force constants in internal coordinates, is diagonalized yielding  $N_{\text{vib}}$  eigenvalues  $\lambda = 4\pi^2\nu$  and  $N_{\text{vib}}$  eigenvectors. If we call the transformation matrix composed of the eigenvectors  $\mathbf{L}$ , then we have

$$\mathbf{L}^\dagger \mathbf{f}_{\text{INT}} \mathbf{L} = \mathbf{\Lambda}, \quad (7)$$

where  $\mathbf{\Lambda}$  is the diagonal matrix with eigenvalues  $\lambda_i$ .

Then the eigenvalues need to be converted into frequencies in units of wavenumbers. First we change from frequencies  $\nu_i$  to wavenumbers  $\tilde{\nu}_i$  via the relationship  $\nu_i = \tilde{\nu}_i \bar{n}$ , where  $\bar{n}$  is the speed of light.

Solving  $\lambda = 4\pi^2 \tilde{\nu}_i^2 \bar{n}^2$  for  $\tilde{\nu}_i^2$ , we obtain

$$\tilde{\nu}_i = \sqrt{\lambda_i / (4\pi^2 \bar{n}^2)}. \quad (8)$$

The rest is simply applying the appropriate conversion factors: from a single molecule to a mole, from hartrees to joules, and from atomic mass units to kilograms.

Combining Eqs. (6) and (7), we arrive at

$$\mathbf{L}^\dagger \mathbf{D}^\dagger \mathbf{f}_{\text{INT}} \mathbf{D} \mathbf{L} = \mathbf{\Lambda} = \mathbf{I}_{\text{MWC}}^\dagger \mathbf{f}_{\text{MWC}} \mathbf{I}_{\text{MWC}}, \quad (9)$$

where  $\mathbf{I} = \mathbf{D} \mathbf{L}$ ;  $\mathbf{I}_{\text{MWC}}$  is determined from calculation of  $\mathbf{I}_{\text{CART}}$ . The elements of the matrix  $\mathbf{I}$  are determined as

$$M_{i,i} = 1/\sqrt{m_i}, \quad (10)$$

$i$  runs over the  $x$ ,  $y$ , and  $z$  coordinates for every atom. The individual elements are given by

$$\mathbf{I}_{\text{CART}_{k,i}} = \sum_j^{3N} \left( \frac{D_{kj} L_{j,i}}{\sqrt{m_j}} \right). \quad (11)$$

The column vectors of these elements, which are normal modes in the Cartesian coordinates, are used for calculating a number of spectroscopic properties, including IR intensities. First of all, once normalized by the procedure described below, they are

displacements in the Cartesian coordinates. Each of the  $3N$  elements of  $\mathbf{I}_{\text{CART}_{k,i}}$  is scaled by normalization factor  $N_i$  for that particular vibrational mode. The normalization is defined by

$$N_i = \sqrt{\left( \sum_k^{3N} I_{\text{CART}_{k,i}}^2 \right)^{-1}}. \quad (12)$$

The reduced mass  $\mu_i$  for the vibrational mode is calculated in a similar way:

$$\begin{aligned} \mu_i &= \left( \sum_k^{3N} I_{\text{CART}_{k,i}}^2 \right)^{-1} = \left[ \sum_k^{3N} \left( \frac{k_{\text{MWC}_{k,i}}}{\sqrt{m_j}} \right)^2 \right]^{-1} = \\ &= \left[ \sum_k^{3N} \left( \frac{k_{\text{MWC}_{k,i}}^2}{m_j} \right) \right]^{-1} = N_i^2. \end{aligned} \quad (13)$$

Note that since  $\mathbf{D}$  is orthonormal, and we can choose  $\mathbf{L}$  to be orthonormal, then  $\mathbf{I}$  is orthonormal as well (Since  $\mathbf{D}^\dagger \mathbf{D} = 1$ ,  $\mathbf{L}^\dagger \mathbf{L} = 1$  then  $\mathbf{I}^\dagger \mathbf{I} = (\mathbf{D} \mathbf{L})^\dagger \mathbf{D} \mathbf{L} = \mathbf{L}^\dagger \mathbf{D}^\dagger \mathbf{D} \mathbf{L} = \mathbf{L}^\dagger \mathbf{1} \mathbf{L} = 1$ ).

There is a difference between the reduced mass calculated in the *ab initio* program and the one calculated using the formula usually used for diatomic molecules:

$$1/\mu = 1/m_1 + 1/m_2. \quad (14)$$

*Ab initio* programs (like GAUSSIAN) use  $k_{\text{MWC}_{k,i}}^2$  rather than 1. Using the elements of  $\mathbf{I}_{\text{MWC}}$  gives consistent results for polyatomic cases, and automatically takes symmetry into consideration.

Simply extending the formula (14) to  $1/\mu = \sum 1/m_i$  would incorrectly yield the same reduced mass for every mode of a polyatomic molecule.

The coordinates used to calculate the force constants, the reduced mass and the Cartesian displacements all are self-consistent. The force constants  $k_i$  are written as  $k_i = 4\pi^2 \tilde{\nu}_i^2 \mu_i$ , since

$$\tilde{\nu} = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}.$$

The force constants are converted from atomic units to millidyne/ångström.

## Discussion

### Energy stability of $\text{XH}_3\text{--H}_2\text{O}$ ( $\text{X} = \text{N}, \text{P}, \text{As}$ ) complexes

The geometry structure of the complexes  $\text{XH}_3\text{--H}_2\text{O}$  ( $\text{X} = \text{N}, \text{P}, \text{As}$ ) (symmetry  $C_s$ ) with the energy of interaction between monomer molecules (MP2/aug-cc-pVDZ):  $\Delta \bar{A} = -6.96$  kcal/mol ( $\text{X} = \text{N}$ );  $\Delta \bar{A} = -2.83$  kcal/mol ( $\text{X} = \text{P}$ ), and (1 P2/6-31++G(d,p):  $\Delta \bar{A} = -7.84$  kcal/mol ( $\text{X} = \text{N}$ );  $\Delta \bar{A} = -3.35$  kcal/mol ( $\text{X} = \text{P}$ );  $\Delta \bar{A} = -3.71$  kcal/mol ( $\text{X} = \text{As}$ ), the

corresponding absolute minimum configuration on the potential energy surface (PES) has a bent intermolecular H-bond (for X = N, P the deviation from linearity is  $\sim 10^\circ$ , which agrees with the data of Ref. 4). In the case of the  $\text{AsH}_3\text{-H}_2\text{O}$  complex, it is possible to speak about almost quasilinear H-bond ( $\sim 2^\circ$ ). The complexes of elements of the VA-group of low-lying periods ( $\text{PH}_3$ ,  $\text{AsH}_3$ ) are less stable as compared to the complex with participation of ammonia.

In formation of complexes, we can notice the following structure changes in the monomers (Tables 2–4): for  $\text{NH}_3\text{-H}_2\text{O}$  the intramolecular

parameters of  $\text{NH}_3$  remain unchanged, while the water molecule is characterized by elongation of the  $\text{H}_1\text{H}_2$  bond (taking part in the formation of H-bonding) by  $0.01 \text{ \AA}$  and increase of the valence angle by  $1.5^\circ$ ; for the  $\text{PH}_3\text{-H}_2\text{O}$  complex one can see (Tables 2–4) insignificant elongation ( $0.003 \text{ \AA}$ ) of the  $\text{H}_1\text{H}_2$  bond and increase of the HPH angle by  $1^\circ$ , for the water molecule in the complex no significant changes occur in the bond lengths and valence angles; for  $\text{AsH}_3\text{-H}_2\text{O}$  (Tables 2, 5, and 6) we can see increase in the valence angle HAsH by  $1^\circ$ , the AsH bond length remains almost unchanged, and for water molecule only  $\text{H}_1\text{H}_2$  changes by  $0.01 \text{ \AA}$ .

Table 2. Geometry and energy parameters of  $\text{H}_2\text{O}$ 

Method	RHF/ 6-31++G(d, p)	RHF/ aug-cc-pVDZ	MP2/ 6-31++G(d, p)	MP2/ aug-cc-pVDZ
Parameter				
$-E$ , a.u.	76.031309	76.041843	76.233376	76.260910
$\mu$ , D	2.2259	1.9636	2.2774	2.0162
$R(\text{OH})$ , $\text{\AA}$	0.943	0.944	0.963	0.966
$\angle\text{HOH}$ , deg	107.2	106.0	105.3	103.9

Note.  $R(\text{OH}) = 0.957 \text{ \AA}$ ;  $\angle\text{HOH} = 104.5^\circ$ ;  $\mu = 1.854$  (Ref. 23).

Table 3. Geometry and energy parameters of  $\text{PH}_3$  and  $\text{NH}_3$ 

Method	RHF/ aug-cc-pVDZ	MP2/ aug-cc-pVDZ	Method	RHF/ aug-cc-pVDZ	MP2/ aug-cc-pVDZ
Parameter			Parameter		
$\text{PH}_3$ ( $\bar{N}_{3v}$ )			$\text{NH}_3$ ( $\bar{N}_{3v}$ )		
$-E$ , a.u.	342.472369	342.614054	$-E$ , a.u.	56.205590	56.404890
$\mu$ , D	0.7676	0.7125	$\mu$ , D	1.5822	1.6413
$R(\text{PH})$ , $\text{\AA}$	1.418	1.427	$R(\text{NH})$ , $\text{\AA}$	1.004	1.020
$\angle\text{HPH}$ , deg	95.5	93.7	$\angle\text{HNH}$ , deg	107.5	106.3
$\angle\text{H}_1\text{H}_3\text{P}_2\text{H}_4$ , deg	96.17	94.0	$\angle\text{H}_1\text{H}_3\text{N}_2\text{H}_4$ , deg	115.6	113.0
$R(\text{PH})^{\text{exp}} = 1.412$ , $\text{\AA}$			$R(\text{NH})^{\text{exp}} = 1.02$ , $\text{\AA}$		
$\angle\text{HPH}^{\text{exp}} = 93.6^\circ$			$\angle\text{HNH}^{\text{exp}} = 107.3^\circ$		

Table 4. Geometry and energy parameters of the complexes  $\text{NH}_3\text{-}\bar{I}_2\bar{I}$  and  $\text{PH}_3\text{-}\bar{I}_2\bar{I}$ 

Method	RHF/ aug-cc-pVDZ	MP2/ aug-cc-pVDZ	Method	RHF/ aug-cc-pVDZ	MP2/ aug-cc-pVDZ
Parameter			Parameter		
$\text{NH}_3\text{-}\bar{I}_2\bar{I}$ ( $\bar{N}_3$ )			$\text{PH}_3\text{-}\bar{I}_2\bar{I}$ ( $\bar{N}_3$ )		
$-E$ , a.u.	132.255238	132.676888	$-E$ , a.u.	418.516763	418.879471
$\mu$ , D	3.4456	3.8783	$\mu$ , D	2.7326	2.6862
$R(\text{NH})$ , $\text{\AA}$	1.004	1.02	$R(\text{PH})$ , $\text{\AA}$	1.417	1.424
$\angle\text{HNNH}$ , deg	107.4	106.4	$\angle\text{HPH}$ , deg	96.2	94.8
	105.4	106.3		96.0	94.7
	105.4	106.3		96.0	94.7
$\angle\text{HOH}$ , deg	106.1	104.5	$\angle\text{HOH}$ , deg	105.8	104.0
$R(\bar{I}\text{H}_i)$ , $\text{\AA}$	0.943	0.965	$R(\bar{I}\text{H}_i)$ , $\text{\AA}$	0.943	0.966
$R(\text{OH}_b)$ , $\text{\AA}$	0.951	0.979	$R(\text{OH}_b)$ , $\text{\AA}$	0.946	0.970
$R(\text{N}\dots\text{O})$ , $\text{\AA}$	3.087	2.939	$R(\text{P}\dots\text{O})$ , $\text{\AA}$	3.919	3.599
$\angle\text{HNNH}_b$ , deg	120.8	120.5	$\angle\text{HPH}_b$ , deg	127.0	129.3
	106.6	108.2		117.3	116.1
	106.6	108.2		117.3	116.1
$\angle\text{NH}_b\text{O}$ , deg	172.7	170.7	$\angle\text{PH}_b\text{O}$ , deg	177.5	168.0
$\angle\text{H}_7\text{NOH}_f$ , deg	-123.3	123.4	$\angle\text{H}_7\text{POH}_f$ , deg	123.1	125.0

Note.  $R(\text{N}\dots\text{H})_{\text{exp}} = 2.983 \text{ \AA}$  (Ref. 21).

Table 5. Geometry and energy parameters of AsH<sub>3</sub>

Method	RHF /	RHF /	MP2/	MP2/
Parameter	6-31G(d, p)	6-31++G(d, p)	6-31G(d, p)	6-31++G(d, p)
-E, a.u.	2233.718274	2233.734738	2233.718107	2233.854811
$\mu$ , D	0.5571	0.5943	0.5035	0.5462
R(AsH), Å	1.501	1.491	1.505	1.494
$\angle$ HAsH, deg	93.7	93.7	92.2	92.455
$\angle$ H <sub>1</sub> H <sub>3</sub> As <sub>2</sub> H <sub>4</sub> , deg	93.9	94.0	92.3	92.565

Note. R(AsH) = 1.511 Å,  $\angle$ HAsH = 92.1° (Ref. 20).

Table 6. Geometry and energy parameters of AsH<sub>3</sub>-H<sub>2</sub>O

Method	RHF /	RHF /	MP2/	MP2/
Parameter	6-31G(d, p)	6-31++G(d, p)	6-31G(d, p)	6-31++G(d, p)
-E, a.u.	2309.745989	2309.770621	2310.062612	2310.094099
$\mu$ , D	2.6204	2.8194	2.3297	2.902
R(AsH), Å	1.499	1.489	1.501	1.492
$\angle$ HAsH, deg	94.6	94.3	92.1	93.1
	94.9	94.7	93.2	93.5
	94.9	94.7	93.2	93.5
$\angle$ HOH, deg	105.7	106.9	103.5	105.1
R( $\bar{I}$ H <sub>f</sub> ), Å	0.943	0.943	0.962	0.963
R(OH <sub>b</sub> ), Å	0.944	0.945	0.962	0.966
R(As...O), Å	4.037	3.960	3.902	3.781
$\angle$ HAsH <sub>b</sub> , deg	141.9	129.8016	175.0	130.8
	110.4	117.8	89.7	118.6
	110.4	117.8	89.7	118.6
$\angle$ AsH <sub>b</sub> O, deg	177.3	178.0	176.7	178.1
$\angle$ H <sub>7</sub> AsOH <sub>f</sub> , deg	128.6	124.2	133.9	124.5

### Intermolecular vibrations of $\bar{O}\bar{I}_3-\bar{I}_2\bar{I}$ complexes

Analysis of normal modes of the NH<sub>3</sub>-H<sub>2</sub>O complex shows that the smallest vibrational frequency of 41 cm<sup>-1</sup> (Å'') can be assigned to the torsion vibration of the NH<sub>3</sub> group, while the frequency of 187 cm<sup>-1</sup> (Å'') can be assigned to the torsion vibration of the H<sub>2</sub>O molecule. The frequency of 176 cm<sup>-1</sup> (Å') corresponds to stretching of the H-bond (N...O). The vibrational frequency of 201 cm<sup>-1</sup> (Å') is determined by bending mode of the NH<sub>3</sub> proton acceptor. The frequencies of 447 (Å') and 727 cm<sup>-1</sup> (Å'') can be assigned to bending vibrations of the H<sub>2</sub>O proton donor.

Analysis of normal mode frequencies of the PH<sub>3</sub>-H<sub>2</sub>O complex shows that the frequency of 23 cm<sup>-1</sup> (Å'') can be assigned to the torsion vibration of the H<sub>2</sub>O molecule, while the frequency of 78 cm<sup>-1</sup> (Å'') can be assigned to the torsion mode of the PH<sub>3</sub> group. The frequency of 93 cm<sup>-1</sup> (Å'') is connected with the bending mode of the PH<sub>3</sub> proton acceptor. Stretching of the H-bond (P...O) corresponds to the frequency of 106 cm<sup>-1</sup> (Å'). The frequencies of 245 (Å') and 397 cm<sup>-1</sup> (Å'') can be assigned to the bending modes of the H<sub>2</sub>O proton donor.

For the AsH<sub>3</sub>-H<sub>2</sub>O complex, the frequency of 20 cm<sup>-1</sup> (Å'') can be assigned to the torsion vibration

of the AsH<sub>3</sub> group, and the frequency of 122 cm<sup>-1</sup> (Å'') – to the torsion vibration of the water molecule. Stretching of the H-bond (As...O) corresponds to the frequency of 74 cm<sup>-1</sup> (Å'). The frequencies of 237 (Å') and 419 cm<sup>-1</sup> (Å'') can be assigned to bending vibrations of the H<sub>2</sub>O proton donor.

### Intramolecular vibrations of $\bar{O}\bar{I}_3-\bar{I}_2\bar{I}$ complexes

Intramolecular bending vibrations of the NH<sub>3</sub> group in the NH<sub>3</sub>-H<sub>2</sub>O complex occur at the frequencies of 1110 (Å'), 1645 (Å') and 1647 cm<sup>-1</sup> (Å''), and the stretching vibrations at 3476 (Å'), 3627 (Å''), and 3629 cm<sup>-1</sup> (Å'). The frequencies of 1662 (Å', bending vibration) and 3579 cm<sup>-1</sup> (Å') can be assigned to intramolecular vibrations of the water molecule; 3895 cm<sup>-1</sup> (Å') corresponds to the bending vibrations of  $\bar{I}\bar{I}$ .

The frequencies of 1007 (Å'), 1152 (Å'), and 1153 cm<sup>-1</sup> (Å'') are assigned to intramolecular bending vibrations of the PH<sub>3</sub> group of the PH<sub>3</sub>-H<sub>2</sub>O complex, while the frequencies of 2465 (Å'), 2483 (Å'), and 2486 cm<sup>-1</sup> (Å'') are assigned to stretches. The intramolecular vibrations of the water molecule are characterized by the frequencies of 1629 cm<sup>-1</sup> (Å', bending vibration) and 3751 cm<sup>-1</sup> (Å'); 3908 cm<sup>-1</sup> (Å') corresponds to  $\bar{I}\bar{I}$  stretches.

The intramolecular bending vibrations of the  $\text{AsH}_3$  group in the  $\text{AsH}_3\text{-H}_2\text{O}$  complex have the frequencies of 1029 ( $\text{A}'$ ), 1242 ( $\text{A}'$ ), and 1243  $\text{cm}^{-1}$  ( $\text{A}''$ ), while the stretches have the frequencies of 2454 ( $\text{A}'$ ), 2477 ( $\text{A}'$ ), and 2459  $\text{cm}^{-1}$  ( $\text{A}''$ ). The frequencies of 1747  $\text{cm}^{-1}$  ( $\text{A}''$ , bending) and 4130  $\text{cm}^{-1}$  ( $\text{A}'$ ) can be assigned to intramolecular modes of the water molecule; 4253  $\text{cm}^{-1}$  ( $\text{A}'$ ) corresponds to  $\bar{1}\bar{1}$  stretches.

Significant changes in the frequencies of intramolecular vibrations at H-bonding were observed

in proton donor, namely, the  $\bar{1}\bar{1}_b$  bond ( $\text{OH}_b - \text{X} \dots \text{O}-\text{H}_b$ ,  $\text{O}-\text{H}_f$  – free valence bond) of the water molecule: for the  $\text{NH}_3\text{-H}_2\text{O}$  complex the displacement  $\Delta\omega = 224 \text{ cm}^{-1}$  with a considerable intensity increase (see Tables 7–9). With a decrease of the interaction energy in the  $\text{PH}_3\text{-H}_2\text{O}$  and  $\text{AsH}_3\text{-H}_2\text{O}$  complexes, these displacements are not so large ( $\sim 20 \text{ cm}^{-1}$ ), but the increase in the band intensity is observed, though not so large as in the  $\text{NH}_3\text{-H}_2\text{O}$  complex.

Table 7. Vibrational frequencies of  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$

Molecule			$\omega, \text{cm}^{-1}$ ( $\text{A}, \text{km/mol}$ )					
			$\text{NH}_3$		$\text{PH}_3$		$\text{AsH}_3$	
Experiment <sup>20</sup>			RHF	MP2	RHF	MP2	RHF	
$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	aug-cc-pVDZ		aug-cc-pVDZ		6-31G(d,p)	6-31++G(d,p)
950	992	906	1104 (172)	1046 (131)	1091 (25)	1008 (18)	1022 (46)	1103 (47)
1628	1122	999	1766 (18)	1649 (13)	1224 (17)	1152 (18)	1155 (21)	1241 (22)
1628	1122	999	1767 (18)	1650 (13)	1224 (17)	1152 (13)	1155 (21)	1241 (22)
3337	2323	2115	3686 (1)	3480 (5)	2525 (40)	2452 (34)	2428 (67)	2443 (156)
3444	2328	2126	3816 (5)	3634 (5)	2528 (87)	2469 (59)	2431 (141)	2444 (156)
3444	2328	2126	3820 (5)	3636 (5)	2528 (87)	2469 (59)	2431 (141)	2461 (85)

Table 8. Harmonic vibrational frequencies of the water molecule  $\omega$ , in  $\text{cm}^{-1}$

Method Symmetry	RHF /	RHF /	MP2/	MP2/	Experiment <sup>20</sup>
	/6-31++G(d, p)	/aug-cc-pVDZ	/6-31++G(d, p)	/aug-cc-pVDZ	
$\text{A}_1$	1728 (114)	1744 (93)	1679 (78)	1622 (67)	1648
$\text{A}_1$	4145 (20)	4130 (14)	3912 (4)	3803 (4)	3832
$\text{B}_2$	4268 (90)	4237 (88)	4050 (34)	3938 (67)	3943

Table 9. Vibrational frequencies of  $\text{NH}_3\text{-}\bar{1}\bar{2}\bar{1}$ ,  $\text{PH}_3\text{-}\bar{1}\bar{2}\bar{1}$ ,  $\text{AsH}_3\text{-H}_2\text{O}$  complexes

$\omega, \text{cm}^{-1}$ ( $\text{A}, \text{km/mol}$ )					
$\text{NH}_3\text{-}\bar{1}\bar{2}\bar{1}$		$\text{PH}_3\text{-}\bar{1}\bar{2}\bar{1}$		$\text{AsH}_3\text{-H}_2\text{O}$	
RHF	MP2	RHF	MP2	RHF	
aug-cc-pVDZ		aug-cc-pVDZ		6-31G(d,p)	6-31++G(d,p)
<i>Frequencies of intermolecular vibrations</i>					
50 (82)	41 (71)	20 (98)	23 (86)	15 (88)	20 (125)
150 (6)	176 (19)	67 (1)	78 (14)	47 (9)	74 (0)
172 (39)	187 (40)	88 (21)	93 (16)	61 (8)	103 (10)
176 (50)	202 (35)	93 (5)	106 (7)	72 (0)	122 (9)
404 (94)	447 (83)	209 (75)	245 (79)	176 (103)	237 (109)
642 (141)	727 (90)	332 (106)	397 (52)	294 (169)	419 (142)
<i>Frequencies of intramolecular vibrations</i>					
1167 (183)	1110 (138)	1090 (35)	1007 (30)	1014 (58)	1029 (61)
1766 (20)	1645 (42)	1223 (15)	1152 (10)	1148 (19)	1243 (19)
1766 (50)	1647 (16)	1224 (17)	1153 (12)	1148 (23)	1243 (25)
1776 (38)	1662 (11)	1752 (67)	1629 (31)	1781 (85)	1747 (84)
3683 (0)	3476 (0)	2534 (41)	2465 (33)	2437 (76)	2454 (130)
3811 (10)	3579 (547)	2538 (69)	2483 (44)	2443 (107)	2459 (128)
3813 (9)	3627 (12)	2540 (70)	2486 (41)	2444 (119)	2477 (78)
4017 (332)	3629 (11)	4110 (87)	3751 (154)	4142 (51)	4130 (90)
4208 (111)	3895 (85)	4223 (154)	3908 (154)	4256 (112)	4253 (159)

### Redistribution of electron density at H-bonding

Consideration of the electron density distribution at formation of complexes (Fig. 1) shows that for the  $\text{NH}_3\text{--H}_2\text{O}$  complex not only the intramolecular charge redistribution (charge flux of  $-0.045e$  from the  $\bar{\Gamma}_b$  atoms to the N atom of the  $\text{NH}_3$  group, for the water molecule) from the  $\bar{\Gamma}_b$  atom to the  $\bar{\Gamma}$  and  $\bar{\Gamma}_f$  atoms  $+0.111e$  is observed, but also the intermolecular charge flux from  $\text{NH}_3$  to  $\text{H}_2\text{O}$   $\Delta Q = 0.07e$ .

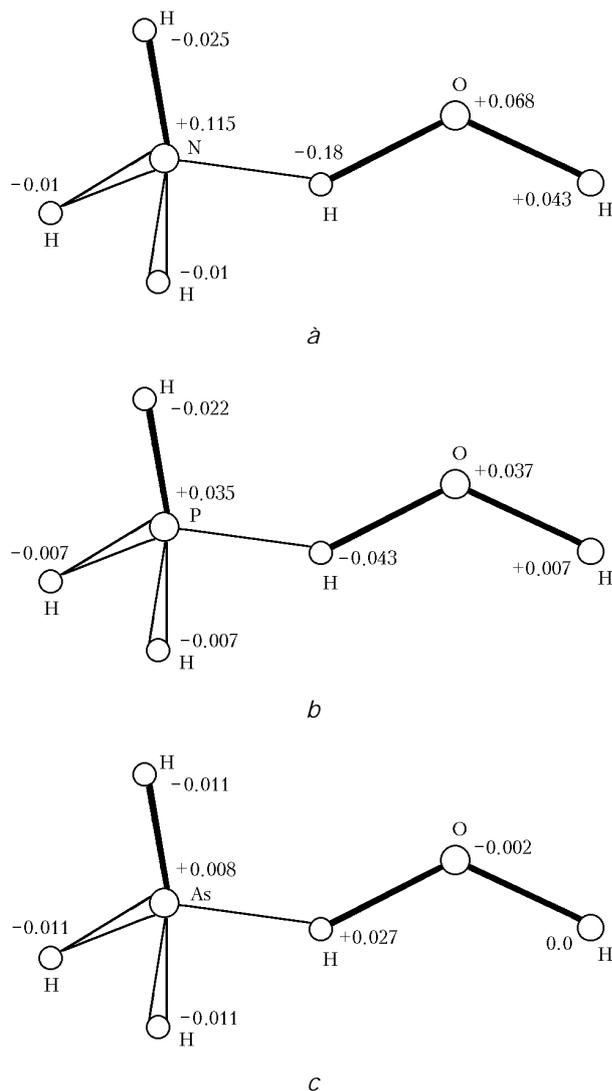


Fig. 1. Geometry structure and changes of the total charge  $Q$  at formation of  $\text{NH}_3\text{--H}_2\text{O}$  (a),  $\text{PH}_3\text{--H}_2\text{O}$  (b), and  $\text{AsH}_3\text{--H}_2\text{O}$  (c) complexes.

For the  $\text{PH}_3\text{--H}_2\text{O}$  complex the intermolecular charge flux is insignificant  $\Delta Q = 0.001e$ , and inside the  $\text{PH}_3$  group the following charge redistribution occurs: charge flux of  $+0.035e$  from the  $\bar{\Gamma}$  atoms to the P atom, and for the water molecule  $-$  charge flux of  $+0.044e$  from the  $\bar{\Gamma}_b$  atom to the  $\bar{\Gamma}$  and  $\bar{\Gamma}_f$  atoms. The  $\text{AsH}_3\text{--H}_2\text{O}$  complex is also characterized by

lower intermolecular charge flux as compared with the  $\text{NH}_3\text{--H}_2\text{O}$  complex  $-\Delta Q = 0.025e$ , the charge is transferred from the  $\text{AsH}_3$  group to  $\text{H}_2\text{O}$ , and intramolecular charge redistribution is the following: the electron density of  $+0.008e$  is transferred from the  $\bar{\Gamma}$  atoms of the  $\text{AsH}_3$  group to the As atom and  $-0.002e$  is transferred from the oxygen atom of the water molecule to the  $\bar{\Gamma}_b$  atom. The high charge flux in the  $\text{NH}_3\text{--H}_2\text{O}$  complex determines the largest increase in the intensity of  $\bar{\Gamma}_b$  vibration.

### Conclusion

Harmonic vibrational frequencies corresponding to the  $\text{OH}_b$  (the  $\bar{\Gamma}$  atom of the hydrogen bridge) stretch are characterized by the largest red shift  $-224\text{ cm}^{-1}$  for the  $\text{NH}_3\text{--H}_2\text{O}$  complex, while for  $\text{PH}_3\text{--H}_2\text{O}$  and  $\text{AsH}_3\text{--H}_2\text{O}$  these shifts are about  $20\text{ cm}^{-1}$ . The intensities corresponding to the  $\bar{\Gamma}_b$  stretch increase by several orders of magnitude at H-bond formation. Analysis of intensity variations through consideration of electron density redistribution reveals that the increase in the intensity of the stretching vibration of the proton donor is primarily determined by the increase in the charge flux at  $\bar{\Gamma}$ -bond formation.

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