STRUCTURE AND FORCE FIELD OF THE NbOCI₃ MOLECULE

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The structure of the NbOCI₃ molecule is studied by electron diffraction at 743(6) K. It is established that the molecule is characterized by C₃ᵥ symmetry and the following structural parameters: rₑ(Nb = O) 1.682(6) Å, rₑ(Nb–Cl) 2.276(5) Å, \( \angle(ONbCl) 107.5(5)° \), and \( \angle(ClNbCl) 111.3(4)° \). Comparison with the other niobium oxytrihalide molecules shows that these values of the Nb = O bond and the bond angles are characteristic. The assignment of the ν₃ frequency of the NbOCI₃ molecule is refined, and the vibration frequencies of the NbOF₃ molecule are estimated.

In this work, we consider the results of the electron diffraction and mass spectrometry studies of niobium oxytrichloride vapors and analyze the structural and vibrational characteristics of the bonds in the NbOX₃ molecules, where X is halogen.

Now the structural parameters of the NbOX₃ (X is halogen) molecules are available for NbOBr₃ [1] and NbOI₃ [2]. Their symmetry (C₃ᵥ) has been reliably established [1, 2].

The vibrational frequencies of gaseous NbOCI₃ were obtained from the IR and Raman spectra [3-5]; the frequencies of NbOI₃ were determined from the electron diffraction data [6].

The IR spectrum of the NbOF₃ vapor was studied in [7]. According to the mass spectrometry data of [7], NbOF₃ was the predominant molecular form in the vapor. Hence, some IR bands were assigned to NbOF₃ assuming that this molecule is of C₃ᵥ symmetry. Later the assignment of the ν₃ and ν₅ bands was refined [8].

The IR spectrum of the NbOBr₃ molecule in the 400-4000 cm⁻¹ range was studied at 200-500°C [9]. The authors of [9] observed only the ν₁ frequency, which corresponds to the Nb = O bond stretching vibrations.

EXPERIMENTAL

The experimental conditions of the electron diffraction analysis are given in Table 1 (for more details, see [10]).

In the first step of the analysis, it is assumed that the vapor contains NbOCI₃ as the only molecular form. The results obtained on this assumption are discussed in [10]. The corresponding radial distribution function \( f(r) \) shows a small maximum at \( r ≈ 1 \) Å. This, together with the noticeable hydrolysis of the substance, suggests that the vapor also involves HCl molecules. The masses detected during the synchronous electron diffraction and mass spectrometry experiments [10] range between 40 and 800 amu; the signal of the HCl molecule does not fall within this range. One of the aims of this work is to check if the vapor of hydrolyzed NbCl₃ involves both HCl and NbOCI₃ molecules during the electron diffraction experiment [10].

The structural parameters are determined by the least-squares analysis of the function of the reduced molecular intensity \( sM(s) \) using the modified program [11] with the minimized functional

\[
Y = \sum W^2 [sM_{exp}(s) - \text{scale} \cdot sM_{theor}(s)]^2,
\]

where \( W^2 \) is the weight function (assumed to be unity) and scale means the scale factor.
TABLE 1. Conditions of the Synchronous Electron Diffraction and Mass Spectrometry Experiments

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle-to-plate distance of the cell (mm)</td>
<td>338</td>
<td>598</td>
</tr>
<tr>
<td>Electron beam current ($\mu$A)</td>
<td>2.5</td>
<td>1.9</td>
</tr>
<tr>
<td>High-speed electron energy (keV)</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Residual pressure in the electron diffraction chamber (mmHg)</td>
<td>$2 \cdot 10^{-6}$</td>
<td>$7 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>Residual pressure in the mass spectrometry unit (mmHg)</td>
<td>$7 \cdot 10^{-7}$</td>
<td>$8 \cdot 10^{-7}$</td>
</tr>
<tr>
<td>Cell temperature (K)</td>
<td>745(3)</td>
<td>741(6)</td>
</tr>
<tr>
<td>Exposure time of a diffraction pattern (s)</td>
<td>120-180</td>
<td>90-100</td>
</tr>
<tr>
<td>Ionizing electron energy (eV)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Number of electron diffraction patterns</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

The theoretical analog of $sM(s)$ includes two terms:

$$sM(s) = \alpha sM(s)_{NbOCl_3} + (1 - \alpha) sM(s)_{HCl}$$

for two molecular forms present in the vapor. The coefficient $\alpha$ is related to the concentrations of different molecules by the equation given in [12].

In this case, the contribution of HCl molecules to the function $sM(s)$ is calculated from the parameters of the HCl molecule ($r_a$ and $l$), which correspond to the temperature of the electron diffraction experiment (467°C). The parameters calculated from the values of the equilibrium internuclear distances and vibration frequency $\omega_v$ [13] are as follows: $r_a(H-Cl) = 1.2894$ Å and $l(H-Cl) = 0.0761$ Å.

The effective parameters are calculated taking into account the corrections for the vibration anharmonicity and the centrifugal extension of the H–Cl bond by the equation [14]

$$r_a = r_e + \langle \Delta \varepsilon \rangle + \delta r - \frac{l^2}{r_e},$$

where $r_e$ is the equilibrium internuclear distance, $\langle \Delta \varepsilon \rangle$ is the term of the anharmonicity of the vibrations of the HCl molecule, and $\delta r$ is the correction for the centrifugal extension. The value of $\langle \Delta \varepsilon \rangle$ is related to the vibration amplitude as follows [14]:

$$\langle \Delta \varepsilon \rangle = \frac{3}{2} a l^2,$$

where $a$ is the Morse anharmonicity constant.

The above parameters of the HCl molecule are constant during the least-squares analysis, while the values of $\alpha$, $r(Nb-O)$, $r(Nb-Cl)$, $\angle(ONbCl)$, and the vibration amplitudes of the NbOCl$_3$ molecule are varied. Other parameters of the NbOCl$_3$ molecule are calculated from geometrical relationships in terms of the $r_a$ structure. Establishing correct relations between the dependent and independent structural parameters of the NbOCl$_3$ molecule requires corrections for perpendicular vibrations ($D$-corrections). To calculate these corrections, we solve an inverse vibrational problem, i.e., using the available frequencies of the NbOCl$_3$ molecule [3-5], we determine (in the valence force field approximation) the force constants, from which the generalized vibration amplitudes are calculated.

As mentioned above, the vibration frequencies of the NbOCl$_3$ molecule are available [3-5]. The interpretations of the vibrational spectra [3-5] are consistent, except for the $\nu_3$ frequency (Table 2).

According to the spectroscopic [3-5] and our preliminary [10] data, the geometry of the molecule corresponds to point group $C_{3v}$, whose vibrational representation is of the form

$$\Gamma_{C_{3v}} = 3A_1 + 3E.$$