HCl, DCl and TCl diatomic molecules in their ground state: the Born-Oppenheimer rovibrational spectra

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Following the first principles the analytic Born-Oppenheimer (B-O) potential curve for the ground state \( X^1\Sigma^+ \) of the molecule (H,D,T)Cl is constructed for whole range of internuclear distances \( R \in [0, \infty) \) for the first time with accuracy 3-4-5 figures in comparison with experimental data where they are available. The procedure is based on matching the perturbation theory at small internuclear distances \( R \) and the multipole expansion at large distances \( R \) into a meromorphic function (two-point Páde approximant) which is fixed by fitting experimental data near the equilibrium configuration. With accuracy of 3-4 figures in the energies, it supports for HCl (DCl, TCl) the 836 (1625, 2366) B-O rovibrational bound states with maximal vibrational number \( \nu_{\text{max}} = 20 \) (29, 36) and maximal angular momentum \( L_{\text{max}} = 64 \) (90, 109) including 24 (46, 63) weakly-bound states (close to dissociation limit) with the energies \( \lesssim 10^{-4} \) Hartree. Insufficiency of available experimental data is indicated and the prediction of missing rovibrational states is made for all three molecules.

I. INTRODUCTION

It is a common knowledge that for diatomic molecule the B-O potential energy curve (saying differently, the electronic term, the dissociation energy curve) is defined as the
eigenvalue of the electronic Hamiltonian, when nuclear masses are assumed to be infinite and the internuclear distance $R$ is \textit{classical}, non-dynamical variable. Naturally, the eigenvalue the B-O potential energy curve depends on $R$ as a parameter and has no dependence on the nuclear masses. Recently \cite{1}, it was proposed to consider the B-O potential energy curve as the result of screening of the Coulomb interaction of two nuclear charges $Z_A, Z_B$, taken as the probes,

$$V(R) = \frac{Z_A Z_B}{R} S(R),$$

where $S(R)$ is the screening function, due to electronic media. At small distances $R$ the screening is negligible, the nuclei repel each other as bare Coulomb charges, while at large $R$ the screening becomes anti-screening: the van der Waals attraction occurs instead of the Coulomb repulsion. Evidently, there exists an instance when the Coulomb repulsion is changed to the van der Waals attraction: at this instance the nuclei do not interact and the potential energy has a minimum. If this minimum is deep enough, the bound states can occur. It manifests the existence of the molecule.

The screening function $S(R)$ is known theoretically in two limiting cases: in the perturbation theory in small $R$ and in the form of multipole expansion (generated by induced moments) at large $R$, modified by the exponentially-small terms for the homonuclear molecules. In \cite{1} it was proposed a certain matching procedure of these three expansions into a single function, which for the case of heteronuclear neutral molecules is realized in the form of two-point Pade approximant $=$ the ratio of two polynomials,

$$S(R) = P(N/N + 5) \equiv \frac{P_N}{Q_{N+5}}.$$

This compact formula was successfully applied to several neutral heteronuclear molecules - HeH \cite{2}, LiH \cite{1}, ClF \cite{3}, H(D,T)F \cite{4} - to find the B-O potential energy curves and its associated B-O rovibrational spectra by solving the nuclear radial Schrödinger equation.

The goal of the present paper is to find the screening function $S(R)$ for the ground state $X^1\Sigma^+$ of the hydrogenic halide $H^{35}\text{Cl}$, and its two isotopologues $D^{35}\text{Cl}$, $T^{35}\text{Cl}$, and calculate the rovibrational spectra for all three systems. The results will be compared with the experimental and theoretical data presented in the summary paper by Coxon-Hajigeorgiou \cite{5}, where the results of practically all previous studies are collected.

It is assumed that the first four figures in rovibrational energies are correction-free: they are not influenced by non-adiabatic (mass corrections), also relativistic and QED corrections
II. POTENTIAL ENERGY CURVE

The hydrogen chloride HCl is made from two heavy nuclei: the proton p and cl-nucleus, and 18 electrons. At large distances between nuclei R (the dissociation limit) it is composed of two neutral atoms: the Hydrogen atom H (Z_H = 1) and the Chlorine atom Cl (Z_Cl = 17). The dissociation energy curve E_d(R) in the lowest energy state of the molecular system is related to total energy E_{total} as

\[ E_d(R) = E_{total}(R) - (E_H + E_{Cl}) , \]

where \( E_H = -0.5 \) a.u. and \( E_{Cl} = -460.148 \) a.u. [8] are the ground state energies of H- and Cl-atoms, respectively. In the united atom limit \( R \to 0 \) the nuclei “glued” into one nucleus and the HCl molecule corresponds to the Argon atom Ar, where the ground state energy is \( E_{Ar} = -527.540 \) a.u. [8]. The dissociation energy \( E_d \) defines the B-O potential energy curve, \( V(R) = E_d \).

It is known that at small internuclear distances \( R \to 0 \) the dissociation energy admits the expansion

\[ E_d = \frac{17}{R} + \varepsilon_0 + 0 \cdot R + O(R^2) , \]

where the first term is the Coulomb repulsion potential \( Z_H Z_{Cl}/R \) and \( \varepsilon_0 \) is the reduced ground state energy of the Argon atom: \( \varepsilon_0 = E_{Ar} + |E_H + E_{Cl}| = -66.892 \) a.u. Following Bingel [9] the linear term \( \sim R \) is absent and the higher order terms can contain \( \log R \), see [10]. The latter can be considered as the indication to the zero radius of convergence of the function \( (E_d - \frac{17}{R}) \) in the expansion at \( R = 0 \).

Following Margenau-Pauling, see [11] and references into it, and also for discussion [12], the behavior of the dissociation energy at large internuclear distances \( R \to \infty \),

\[ E_d = -\frac{C_6}{R^6} + \frac{C_8}{R^8} + \cdots , \]

corresponds to multipole expansion of induced moments Present authors are not familiar with the statement about the radius of convergence of this expansion at \( 1/R = 0 \). Here...
$C_6 = 23.41$ a.u. is the van der Waals constant, based on the fit of the \textit{ab initio} calculations. Note that although this value differs from the Slater-Kirkwood estimate $C_6 = 23.62$ a.u., they are in agreement of $< 1\%$, see for discussion [5]: this difference does not lead to qualitative consequences for B-O rovibrational spectra, four significant figures remain unchanged. Matching the expansions (2) and (3) into a single function leads naturally to the B-O potential energy curve in the form of two-point Pade approximant,

$$E_d(R) = \frac{1}{R} \text{Pade}[N/N + 5](R)_{n_0, n_\infty} \equiv \frac{1}{R} \frac{P_N}{Q_{N+5}},$$

(4)

where $P, Q$ are polynomials in $R$, here $n_0$ is the number of coefficients in the expansion (2) which we want to reproduce exactly, while $n_\infty$ is the number of coefficients which are reproduced exactly at $R = \infty$ in the expansion (3). Following [1] we will call the potential (4) the Turbiner-Olivares (TO) potential.

In the first attempt to construct the B-O potential curve we choose $N = 1$ in (4)

$$E_d^{(1)}(R) = \frac{1}{R} \text{Pade}[1/6](R)_{2,1} =$$

$$\frac{1}{R} \frac{17 - a_1 R}{1 - \frac{(a_1 + a_2)}{17} R + b_2 R^2 + b_3 R^3 + b_4 R^4 + b_5 R^5 + \frac{a_4}{C_6} R^6},$$

(5)

where five free parameters are fixed as following

$$a_1 = 9.907, \ b_2 = 19.493, \ b_3 = -30.706, \ b_4 = 17.952, \ b_5 = -4.480,$$

and $C_6 = 23.41$ a.u. This simple expression (5) allows us to reproduce three significant figures in all available experimental and theoretical data on the potential curve collected in [5]. However, in order to increase the accuracy to reproduce four (or more) significant figures with five conditions on the coefficients in the expansions imposed: $n_0 = 3, n_\infty = 2$, the higher order Páde approximants must be considered.

In making the concrete calculations it was tried $N = 3,4,5$. It is worth noting the following technical moment. Since $E_d$ is known in discrete points in $R$, two extra requirements were ”enforced” in order to find $S(R)$: (i) the polynomial $Q(R)$ in (4) has no roots at $R > 0$ and (ii) complex roots of $Q(R)$ (when exist) should be characterized by sufficiently large imaginary parts in order to guarantee a smooth behavior of the potential energy curve at positive $R$. Eventually, we arrive at the fitting function (4) with $N = 5$ of the form

$$E_d^{(2)}(R) = \frac{1}{R} \frac{17 + \sum_{i=1}^{4} a_i R^i - a_5 R^5}{1 + \alpha_1 R + \alpha_2 R^2 + \sum_{i=3}^{8} b_i R^i - \alpha_3 R^9 + \alpha_4 R^{10}},$$

(6)
with the following constraints on coefficients imposed

\[
\begin{align*}
\alpha_1 &= (a_1 - \varepsilon_0)/17 , \\
\alpha_2 &= (\varepsilon_0^2 + 17 a_2 - a_1 \varepsilon_0)/17^2 , \\
\alpha_3 &= a_4 b_8/a_5 , \\
\alpha_4 &= a_5/C_6 ,
\end{align*}
\]

which guarantees that the three analytically known coefficients in front of \(R^{-1}\), \(R^0\) and \(R\) terms at small internuclear distances (2) and the two coefficients in front of \(R^{-6}\) and \(R^{-7}\) for large internuclear distances (3) are reproduced exactly. Remaining 11 parameters in (6) are assumed to be free. These parameters are fixed by making a fit of experimental data on the ground state potential energy curve, presented in [5]; their explicit values are

\[
\begin{align*}
a_1 &= 327.321 , & b_3 &= 33.7337 , \\
a_2 &= 133.987 , & b_4 &= -31.2621 , \\
a_3 &= -275.248 , & b_5 &= -7.72363 , \\
a_4 &= 54.4855 , & b_6 &= 61.8757 , \\
a_5 &= 3.611634 , & b_7 &= -44.2838 , \\
& & b_8 &= 14.4997 ,
\end{align*}
\]

leading to the accuracy of 4-5 significant figures. It implies that the spectroscopic constants are reproduced with a similar accuracy. Alternately, three out of 11 parameters in (8) can be fixed by requirement to reproduce 4-5 significant figures for the equilibrium distance, dissociation energy at equilibrium and zero vibrational energy (the curvature of the potential well at minimum). It must be emphasized that in order to fix the 11 parameters (8) in general it is enough to know experimental data and/or the results of the \textit{ab initio} calculations in 11 points in \(R\) only.

Table I presents the dissociation energy \(E_d^{(2)}\) vs. \(R\), derived from the analytic expression (6) with parameters (7)-(8) for different internuclear distances \(R\). They are compared with experimental data and their phenomenological interpretation, see [5]: as can be seen that except for a few points not less than 4 decimal digits are reproduced. Fit (6) is depicted in Fig. 1 together with experimental points, wherever they are available [5]. It must be emphasized that such a quality of the description via (6) does not require to introduce phenomenologically the terms \(\sim (m_e/m_p)\) and \(\sim (m_e/m_cl)\) into B-O potential curve as was
done in [5], see Eq.(3). Theoretically, the appearance of these terms contradicts to the founding principles of the Born-Oppenheimer approximation.

The minimum of the potential energy curve \( E_d^{(2)}(R) \) is calculated by taking the derivative of (6) and making it vanishing, \( dE_d^{(2)}(R)/dR = 0 \). As the result \( R_{\text{min}} = 2.408542 \) a.u. and \( E_{\text{min}} = -0.16960 \) Hartree, which is in excellent agreement with the values \( R_{\text{equilibrium}} = 2.408544 \) a.u. and \( E_{\text{equilibrium}} = -0.169641 \) Hartree [5].

![FIG. 1: Potential (dissociation) energy \( E \) of the ground state \( X^1\Sigma^+ \) for the (H,D,T)Cl molecule vs. internuclear distance \( R \): (i) the Padé approximant (6) (red solid line), (ii) experimental data [5] (red bullets), (iii) blue diamonds - prediction by (6), (iv) at \( R = 1.71757 \) a.u. the energy \( E = 0 \).](image)

### III. B-O ROVIBRATIONAL SPECTRA

In the standard Born-Oppenheimer approximation scheme, the rovibrational spectrum of HCl is found by solving the nuclear (radial) Schrödinger equation

\[
\left[ -\frac{1}{\mu_h} \frac{d^2}{dR^2} + \frac{L(L+1)}{\mu_h R^2} + V(R) \right] \phi(R) = E_{\nu,L} \phi(R),
\]

searching for the square-integrable eigenfunctions. Here \( \mu_h = m_{\text{Cl}} m_{\text{H}} / (m_{\text{Cl}} + m_{\text{H}}) \) is the reduced mass for chlorine and hydrogen nuclei, \( L \) is the angular momentum; \( E_{\nu,L} \) is the
TABLE I: Dissociation energy $E_d^{(2)}$ in Hartree for the ground state $X^1\Sigma^+$ for HCl as a function of the internuclear distance $R$ in two regimes: from small $R$ to equilibrium and from large $R$ to equilibrium. 2nd and 5th columns are experimental (and phenomenological) data from [5]. 3rd and 6th columns are from (6).

| $R_{\text{min}}$ | $E_{d_{\text{min}}}^{R_{\text{min}}} [5]$ | $E_{d_{\text{min}}}^{R_{\text{min}}} (6)$ | $R_{\text{max}}$ | $E_{d_{\text{max}}}^{R_{\text{max}}} [5]$ | $E_{d_{\text{max}}}^{R_{\text{max}}} (6)$ |
|------------------|-------------------------------|-------------------------------|------------------|-------------------------------|-------------------------------|
| 1.717716 | -0.000082 | -0.00011 | 8.825021 | -0.000082 | -0.00007 |
| 1.719071 | -0.001031 | -0.00105 | 6.585696 | -0.001031 | -0.00105 |
| 1.722427 | -0.003364 | -0.00338 | 5.855864 | -0.003364 | -0.00341 |
| 1.727531 | -0.006866 | -0.00688 | 5.437063 | -0.006866 | -0.00687 |
| 1.734145 | -0.011318 | -0.01132 | 5.134002 | -0.011318 | -0.01128 |
| 1.742171 | -0.016584 | -0.01658 | 4.890604 | -0.016584 | -0.01655 |
| 1.751549 | -0.022571 | -0.02256 | 4.683618 | -0.022571 | -0.02256 |
| 1.762308 | -0.029214 | -0.02920 | 4.500867 | -0.029214 | -0.02922 |
| 1.774500 | -0.036461 | -0.03645 | 4.335109 | -0.036461 | -0.03649 |
| 1.788227 | -0.044276 | -0.04426 | 4.181679 | -0.044276 | -0.04430 |
| 1.803636 | -0.052627 | -0.05261 | 4.037339 | -0.052627 | -0.05264 |
| 1.820931 | -0.061495 | -0.06148 | 3.899720 | -0.061495 | -0.06149 |
| 1.840391 | -0.070860 | -0.07085 | 3.766980 | -0.070860 | -0.07084 |
| 1.862397 | -0.080712 | -0.08071 | 3.637572 | -0.080712 | -0.08068 |
| 1.887477 | -0.091041 | -0.09105 | 3.510072 | -0.091041 | -0.09101 |
| 1.916400 | -0.101842 | -0.10186 | 3.383033 | -0.101842 | -0.10183 |
| 1.950315 | -0.113112 | -0.11313 | 3.254758 | -0.113112 | -0.11311 |
| 1.991106 | -0.124850 | -0.12488 | 3.122935 | -0.124850 | -0.12487 |
| 2.042201 | -0.137055 | -0.13708 | 2.983789 | -0.137055 | -0.13709 |
| 2.111183 | -0.149731 | -0.14974 | 2.829445 | -0.149731 | -0.14975 |
| 2.224536 | -0.162880 | -0.16286 | 2.633188 | -0.162880 | -0.16287 |
| 2.408544 | -0.169641 | -0.16960 | 2.370104 | -0.169641 | -0.16960 |

rovibrational energy of the state with vibrational and rotational quantum numbers $\nu$ and
The nuclear potential \( V(R) = E_d \) is the electronic energy curve given by (6). Nowadays, equation (9) can be easily solved numerically with any desired accuracy, in particular, by using the so-called Lagrange-Mesh Method [13] (for the code written in Fortran-90, see [3], the ArXiv version). Nuclear masses are chosen as \( m_H = 1836.15267 \) [14] for H and \( m_{Cl} = 63727.3189 \) for \(^{35}\text{Cl} \) [15], measured in the mass of electron.

The obtained B-O vibrational spectra \( E_{\nu,0} \) of the bound states is presented in Table II. In total, there are 21 vibrational states \( (\nu = 0, \ldots, 20) \): this amount is in agreement with numbers presented in [5]. Comparison with the 21 vibrational energies reported in [5] shows the coincidence in 4 d.d. Note that the energy \( E_{20,0} \) of the bound state \((20,0)\) is close to the dissociation threshold being smaller than \( 10^{-4} \) Hartree. Thus, it is a weakly-bound state. Its existence is certainly questionable depending upon the values of corrections.

The complete rovibrational spectra is depicted in the histogram in Fig. 2. In total, there are 836 B-O rovibrational states with \( \nu_{\max} = 20 \) and \( L_{\max} = 64 \). In general, there are 7 states with the energy \( \lesssim 10^{-4} \) Hartree and additionally 17 states whose energies are of order of \( \sim 10^{-4} \) Hartree - they are marked by dots and stars, respectively, in the histogram. States above the red continuous line are of positive energy, thus, they are quasi-bound states. These are presented in the phenomenological analysis [5] as well as in experimental data which are beyond the present B-O analysis. Note that from one side, these quasi-bound states are the artifacts of the modification of the nuclear Schrödinger equation (9) presented in [5], see Eqs.(1)-(3), and, from another side, they come from experimental data. The energy \( E_{17,23} \), labeled by ”?” in the histogram, is indicated in [5] as bound: it is not supported in the present calculation. It must be emphasized that 57 B-O rovibrational states predicted for \( L = 50 - 64 \) are absent in experimental data as well as 26 highly excited B-O rovibrational states for \( L = 1 - 14 \).

The same B-O potential energy curve (6) can be used to calculate the B-O rovibrational spectra of the HCl isotopologies: the deuteron chloride DCl and the triton chloride TCl. It implies the appropriate change of the reduced mass in the nuclear Schrödinger equation (9),

\[
\mu_h \rightarrow \mu_d = \frac{m_{Cl} m_D}{(m_{Cl} + m_D)},
\]
or

\[
\mu_h \rightarrow \mu_t = \frac{m_{Cl} m_T}{(m_{Cl} + m_T)},
\]
TABLE II: B-O vibrational energies $E_{\nu,0}$ in Hartree for the ground state $X^1\Sigma^+$ of the HCl molecule. Vibrational energies from [5] are presented in 3rd column.

| $\nu$ | $E_{\nu,0}$ | [5] |
|-------|-------------|-----|
| 0     | -0.16285    | -0.162880 |
| 1     | -0.14972    | -0.149731 |
| 2     | -0.13705    | -0.137055 |
| 3     | -0.12485    | -0.124850 |
| 4     | -0.11311    | -0.113112 |
| 5     | -0.10183    | -0.101842 |
| 6     | -0.09102    | -0.091041 |
| 7     | -0.08068    | -0.080712 |
| 8     | -0.07083    | -0.070860 |
| 9     | -0.06147    | -0.061495 |
| 10    | -0.05260    | -0.052627 |
| 11    | -0.04425    | -0.044276 |
| 12    | -0.03644    | -0.036461 |
| 13    | -0.02919    | -0.029214 |
| 14    | -0.02255    | -0.022571 |
| 15    | -0.01655    | -0.016584 |
| 16    | -0.01128    | -0.011318 |
| 17    | -0.00684    | -0.006866 |
| 18    | -0.00336    | -0.003364 |
| 19    | -0.00104    | -0.001031 |
| 20    | -0.00007    | -0.000082 |

respectively. Here $m_{D,T}$ are masses of deuteron $m_D = 3670.48297 \text{ } m_e$ and triton $m_T = 5496.92154 \text{ } m_e$, respectively, see [14].

In Tables IV and V the comparison of the vibrational states for DCl and TCl is presented: in general, there is a coincidence in 4 d.d. with experimental data. The highest vibrational
TABLE III: B-O rotational energies $E_{0,L}$ in Hartree for the ground state $X^1\Sigma^+$ of the HCl molecule for $L = 0, \cdots, 64$ compared with experimental and theoretical data from [5].

| $L$ | $E_{0,L}$ | [5] | $L$ | $E_{0,L}$ | [5] | $L$ | $E_{0,L}$ | [5] |
|-----|-----------|-----|-----|----------|-----|-----|----------|-----|
| 0   | -0.16285  | -0.162880 | 22  | -0.13938 | -0.139417 | 44  | -0.07755 | -0.077592 |
| 1   | -0.16275  | -0.162785 | 23  | -0.13730 | -0.137343 | 45  | -0.07407 | -0.074115 |
| 2   | -0.16256  | -0.162595 | 24  | -0.13515 | -0.135189 | 46  | -0.07055 | -0.070594 |
| 3   | -0.16228  | -0.162310 | 25  | -0.13292 | -0.132957 | 47  | -0.06699 | -0.067032 |
| 4   | -0.16190  | -0.161930 | 26  | -0.13061 | -0.130647 | 48  | -0.06338 | -0.063430 |
| 5   | -0.16142  | -0.161456 | 27  | -0.12822 | -0.128262 | 49  | -0.05975 | -0.059791 |
| 6   | -0.16086  | -0.160887 | 28  | -0.12576 | -0.125802 | 50  | -0.05607 | -0.056117 |
| 7   | -0.16019  | -0.160224 | 29  | -0.12323 | -0.123269 | 51  | -0.05236 |
| 8   | -0.15944  | -0.159468 | 30  | -0.12062 | -0.120664 | 52  | -0.04863 |
| 9   | -0.15859  | -0.158619 | 31  | -0.11795 | -0.117989 | 53  | -0.04486 |
| 10  | -0.15764  | -0.157677 | 32  | -0.11520 | -0.115246 | 54  | -0.04107 |
| 11  | -0.15661  | -0.156643 | 33  | -0.11239 | -0.112435 | 55  | -0.03725 |
| 12  | -0.15548  | -0.155518 | 34  | -0.10951 | -0.109560 | 56  | -0.03341 |
| 13  | -0.15427  | -0.154302 | 35  | -0.10951 | -0.106621 | 57  | -0.02955 |
| 14  | -0.15296  | -0.152996 | 36  | -0.10357 | -0.103619 | 58  | -0.02567 |
| 15  | -0.15157  | -0.151601 | 37  | -0.10051 | -0.100558 | 59  | -0.02178 |
| 16  | -0.15008  | -0.150118 | 38  | -0.09739 | -0.097438 | 60  | -0.01787 |
| 17  | -0.14851  | -0.148547 | 39  | -0.09422 | -0.094261 | 61  | -0.01395 |
| 18  | -0.14685  | -0.146890 | 40  | -0.09098 | -0.091030 | 62  | -0.01003 |
| 19  | -0.14511  | -0.145148 | 41  | -0.08770 | -0.087745 | 63  | -0.00610 |
| 20  | -0.14328  | -0.143320 | 42  | -0.08436 | -0.084410 | 64  | -0.00216 |
| 21  | -0.14137  | -0.141410 | 43  | -0.08098 | -0.081025 |

energies $E_{29,0}$ for DCl and $E_{35,0}$ for TCl, respectively, are smaller than $10^{-4}$ Hartree, hence, they are close to the dissociation threshold. They should be excluded. Besides that the vibrational energies $E_{28,0}$ for DCl and $E_{34,0}$ for TCl are of the order of $10^{-4}$ Hartree: their
FIG. 2: Rovibrational spectra for the ground state $X^1\Sigma^+$ of the hydrogen chloride HCl - the histogram - predicted in the potential (6). The 7 states with energy $< 10^{-4}$ Hartree are marked by dots and the 17 states whose energies are of order $\sim 10^{-4}$ Hartree are marked by stars. The rovibrational states (marked by blue) are the results from [5]. Those states which are above the red continuous line are the artifacts of the phenomenological analysis performed in [5], they are of positive energies. The state $(17, 23)$ with the energy $E_{\nu, L} = E_{17, 23}$, labeled by ”?” , is indicated as bound in [5]: it is not confirmed in present calculation. All B-O states with $L = 51 - 64$ are missing in experimental data in [5].

existence is questionable, the corrections can be of the same order of magnitude. Note that the maximal number of the vibrational states is increased from 19 for HCl to 28 for DCl and 34 for TCl, respectively, see Table VI. In a similar way the maximal number of the rotational states is increased from 64 for HCl to 90 for DCl and 109 for TCl, respectively, see Table VI.

For DCl the complete rovibrational spectra is depicted in the histogram in Fig. 3. In total, there are 1625 B-O rovibrational states with $\nu_{\text{max}} = 29$ and $L_{\text{max}} = 90$. In general, there are 8 states with the energy $\lesssim 10^{-4}$ Hartree and additionally 38 states whose energies are of
FIG. 3: Rovibrational spectra for the ground state \( X^1\Sigma^+ \) of the deuteron chloride DCl - the histogram - predicted in the potential \( (6) \). The 8 states (including 2 for \( L = 0 \)) with energy < \( 10^{-4} \) Hartree marked by dots and the 38 states (including 1 for \( L = 0 \)) whose energies are of order \( \sim 10^{-4} \) Hartree marked by stars. The rovibrational states (marked by blue) are the experimental and theoretical results from \( [5] \). Those states which are above the red continuous line are the artifacts of the phenomenological analysis \( [5] \), they are of positive energies. All 157 states with \( L = 66 - 90 \) are missing in experimental and theoretical data \( [5] \) as well as 53 states with \( L = 1 - 21 \).

order of \( \sim 10^{-4} \) Hartree - in the histogram, they are marked by dots and stars, respectively. States above the red continuous line have positive energy, thus, they are quasi-bound states. These are presented in the phenomenological analysis \( [5] \) as well as experimental data which are not confirmed in the present B-O analysis. From one side, they are the artifacts of the modification of the nuclear Schrödinger equation \( (9) \) presented in \( [5] \), see Eqs.(1)-(3), and, from another side, they come from experimental data. It must be emphasized that 160 B-O rovibrational states predicted for \( L = 65 - 90 \) are absent in experimental data as well as 53 highly excited B-O rovibrational states for \( L = 1 - 21 \).
FIG. 4: B-O rovibrational spectra for the ground state $X^1\Sigma^+$ of the triton chloride TCl - the histogram - predicted in the potential \((6)\). The 15 states (including two with $L = 0$) with energy $< 10^{-4}$ Hartree marked by dots and the 48 states (including one with $L = 0$) whose energies are of order $\sim 10^{-4}$ Hartree marked by stars. The rovibrational states (marked by blue) are the experimental (and phenomenological) results from \([5]\). Almost all 2071 B-O rovibrational states with $L = 1 - 109$ are missing in experimental (and phenomenological) data \([5]\).

For TCl the complete rovibrational spectra is depicted in the histogram in Fig. 4. In total, there are 2366 B-O rovibrational states with $\nu_{\text{max}} = 36$ and $L_{\text{max}} = 109$. In general, there are 15 states with the energy $\lesssim 10^{-4}$ Hartree and additionally 48 states whose energies are of order of $\sim 10^{-4}$ Hartree - they are marked by dots and stars, respectively, in the histogram. There are 3 vibrational states with the energies $\lesssim 10^{-4}$ Hartree. It must be emphasized that 2071 B-O rovibrational states are predicted for $L = 1 - 109$ - almost all of them are absent in experimental (and phenomenological) data.
TABLE IV: Vibrational energies $E_{\nu,0}$ in Hartree for the ground state $X^1\Sigma^+$ of the DCl molecule. Experimental and theoretical data for energies of the vibrational states [5] are presented in 3rd and 5th columns. Energies $E_{28,0}$ and $E_{29,0}$ are beyond of the present accuracy.

| $\nu$ | $E_{\nu,0}$  | [5] $E_{\nu,0}$ | [5] |
|-------|---------------|-----------------|-----|
| 0     | -0.164749    | -0.164767       |     |
| 1     | -0.155238    | -0.155240       |     |
| 2     | -0.145966    | -0.145957       |     |
| 3     | -0.136932    | -0.136917       |     |
| 4     | -0.128136    | -0.128119       |     |
| 5     | -0.119578    | -0.119562       |     |
| 6     | -0.111258    | -0.111246       |     |
| 7     | -0.103178    | -0.103170       |     |
| 8     | -0.095338    | -0.095335       |     |
| 9     | -0.087740    | -0.087742       |     |
| 10    | -0.080387    | -0.080393       |     |
| 11    | -0.073281    | -0.073289       |     |
| 12    | -0.066425    | -0.066434       |     |
| 13    | -0.059824    | -0.059832       |     |
| 14    | -0.053481    | -0.053488       |     |
| 15    | -0.047403    | -0.047408       |     |
| 16    | -0.041596    | -0.041599       |     |
| 17    | -0.036069    | -0.036072       |     |
| 18    | -0.030833    | -0.030837       |     |
| 19    | -0.025901    | -0.025908       |     |
| 20    | -0.021289    | -0.021301       |     |
| 21    | -0.017018    | -0.017038       |     |
| 22    | -0.013116    | -0.013143       |     |
| 23    | -0.009615    | -0.009646       |     |
| 24    | -0.006562    | -0.006588       |     |
| 25    | -0.004010    | -0.004024       |     |
| 26    | -0.002033    | -0.002033       |     |
| 27    | -0.000712    | -0.000718       |     |
| 28    | -9.E(-9)     | -2.E(-6)        |     |
| 29    | -9.E(-9)     | -2.E(-6)        |     |

IV. CONCLUSIONS

Using the physics arguments [1] and experimental data in vicinity of the equilibrium configuration the Born-Oppenheimer potential energy curve for the ground state $X^1\Sigma^+$ of the (H,D,T)Cl molecules is constructed in the form of ratio of two polynomials in the whole range of internuclear distances. By making comparison with experimental (and phenomenological) data one can see that the constructed curve is in agreement in 3-4-5 figures. This curve, when used as a potential in the nuclear radial Schrödinger equation, allows us to calculate the
TABLE V: Vibrational energies $E_{\nu,0}$ in Hartree for the ground state $X^{1}\Sigma^{+}$ of the TCl molecule. Experimental and theoretical data for energies of the vibrational states [5] are presented in the 3rd and 5th columns. Values $E_{34,0}$ and $E_{35,0}$ are beyond the present accuracy.

| $\nu$ | $E_{\nu,0}$  | $E_{\nu,0}$ [5] | $\nu$ | $E_{\nu,0}$  | $E_{\nu,0}$ [5] |
|-------|--------------|-----------------|-------|--------------|-----------------|
| 0     | -0.165579    | -0.165593       | 18    | -0.048473    | -0.048472       |
| 1     | -0.157668    | -0.157668       | 19    | -0.043603    | -0.043601       |
| 2     | -0.149921    | -0.149910       | 20    | -0.038924    | -0.038921       |
| 3     | -0.142338    | -0.142320       | 21    | -0.034440    | -0.034437       |
| 4     | -0.134918    | -0.134896       | 22    | -0.030157    | -0.030156       |
| 5     | -0.127661    | -0.127638       | 23    | -0.026084    | -0.026087       |
| 6     | -0.120568    | -0.120545       | 24    | -0.022231    | -0.022238       |
| 7     | -0.113638    | -0.113617       | 25    | -0.018608    | -0.018622       |
| 8     | -0.106871    | -0.106855       | 26    | -0.015229    | -0.015250       |
| 9     | -0.100270    | -0.100257       | 27    | -0.012114    | -0.012140       |
| 10    | -0.093833    | -0.093825       | 28    | -0.009281    | -0.009310       |
| 11    | -0.087563    | -0.087559       | 29    | -0.006758    | -0.006785       |
| 12    | -0.081461    | -0.081460       | 30    | -0.004576    | -0.004595       |
| 13    | -0.075528    | -0.075529       | 31    | -0.002775    | -0.002782       |
| 14    | -0.069766    | -0.069768       | 32    | -0.001400    | -0.001403       |
| 15    | -0.064177    | -0.064179       | 33    | -0.000498    | -0.000515       |
| 16    | -0.058763    | -0.058765       | 34    | -0.000077    | -0.000108       |
| 17    | -0.053527    | -0.053528       | 35    | -4.E(-7)     | -6.E(-6)        |

B-O rovibrational spectra for all three molecules HCl, DCl, TCl exploiting the dependence on the reduced mass of nuclei ONLY. By comparing the B-O rovibrational energies with available experimental and theoretical data one can see the general agreement in 4-5 figures (or better). In particular, there is an excellent agreement with description of vibrational states of all three molecules HCl, DCl, TCl. It defines the domain of applicability of the
TABLE VI: $\nu_{\text{max}}$ and $L_{\text{max}}$ for the systems HCl, DCl and TCl obtained in the present work. The numbers in brackets (20), (29) and (36) indicate the total number of vibrational states, which includes the states with energy $< 10^{-4}$ Hartree

|     | $\nu_{\text{max}}$ | $L_{\text{max}}$ | Total # | $\mu$     |
|-----|---------------------|-------------------|---------|-----------|
| HCl | 19 (20)             | 64                | 836     | 1784.7299 |
| DCl | 28 (29)             | 90                | 1625    | 3470.5885 |
| TCl | 33 (36)             | 109               | 2366    | 5060.4249 |

Born-Oppenheimer approximation, which is free of corrections of any kind.

Obtained results indicate that a lot of experimental information is missing: they can be considered as a prediction of the existence of many highly-excited rovibrational bound states, in particular, with large angular momentum. It should be emphasized that the situation is extremely poor about rovibrational spectra of TCI molecule.

Similar program was realized for HF, DF, TF molecules, see [4], with analogous conclusions: a lot of experimental information is missing and predictions about it are made.

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