ClF diatomic molecule: rovibrational spectra

Horacio Olivares-Pilón∗

Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa,
Apartado Postal 55-534, 09340 México, D.F., Mexico

Alexander V. Turbiner†

Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México,
Apartado Postal 70-543, 04510 México, D.F., Mexico

(Dated: May 11, 2022)

Following the first principles the analytic Born-Oppenheimer (BO) potential curve for the ground state \(X^1\Sigma^+\) of the molecule ClF is proposed for whole range of internuclear distances \(R \in [0, \infty)\). It is based on matching the perturbation theory at small internuclear distances \(R\) and multipole expansion at large distances \(R\), it has the form of two-point Pade approximant and provides 3-4 figures in rovibrational energies. It supports 5719 rovibrational states with maximal vibrational number \(\nu_{\text{max}} = 47\) and maximal angular momentum \(L_{\text{max}} = 210\) including 36 weakly-bound states close to threshold (to dissociation limit) with the energies \(\lesssim 10^{-4}\) hartree. The van der Waals constant \(C_6^{\text{(ClF)}} \sim 29.3\) a.u. is predicted.

I. INTRODUCTION

The chlorine monofluoride ClF, a heteronuclear diatomic molecule composed of two halogens, Cl and F, was studied experimentally for the first time in 1942 [1]. 32 years later in 1974, the first theoretical work on this molecule was published [2]. Since then, the molecule ClF has been the subject of numerous experimental and theoretical investigations (see e.g. [3–6] and references therein). This system is among of diatomic interhalogens, which since long ago is of interest of laser physics [7, 8] with a chance to lead to a new type of gas lasers. At room temperature, ClF is a colorless gas, which is highly reactive and corrosive [9]. Needless to say that the presence of the 26 electrons and two heavy nuclei makes chlorine monofluor-
ride molecule an extremely complex object to study theoretically in traditional approaches. Recently, it was proposed a new approach based on matching perturbation theory at small distances and multipole expansion at large distances \cite{10}, which does not rely heavily on massive \textit{ab initio} calculations. In this approach the nucleus play the role of \textit{probs} and BO potential curve has a meaning of screening function of Coulomb interaction in electronic media. In the past it was successfully checked for \( \text{H}_2^+ \), \( \text{HeH} \) and \( \text{H}_2 \) diatomics \cite{11,12}, while in \cite{10} it is illustrated by studying \( \text{He}_2^+ \) and LiH.

This Note will be dedicated to study the ground state BO potential curve of ClF molecule for all internuclear distances. It is assumed that the first four figures in energy are correction-free: they are not influenced by adiabatic, also relativistic and QED corrections and any other corrections like it is for Helium-like and Lithium-like ionic sequences in atomic physics \cite{13}.

\section{II. Potential Energy Curve}

The chlorine monofluoride ClF is composed of a Chlorine atom Cl (\( Z_{\text{Cl}} = 17 \)) and a Fluorine atom F (\( Z_{\text{F}} = 9 \)). The dissociation energy \( E_d \) is related with total energy \( E(R) \) as

\begin{equation}
E_d = E(R) - (E_{\text{Cl}} + E_{\text{F}}),
\end{equation}

where the ground state energies \( E_{\text{Cl}} = -460.148 \) hartree and \( E_{\text{F}} = -99.7339 \) hartree \cite{14} are taken. The united atom limit of the ClF molecule corresponds to the Iron atom Fe, where the ground state energy is equal to \( E_{\text{Fe}} = -1242.985 \) hartree \cite{14}, it can be considered as a “splitting” of \((\text{Fe})\) nucleus to \((\text{Cl})\) plus \((\text{F})\) nuclei.

For small internuclear distances \( R \to 0 \) the dissociation energy behaves as

\begin{equation}
E_d = \frac{153}{R} + \varepsilon_0 + 0 \cdot R + O(R^2),
\end{equation}

where the first term is the Coulomb repulsion \( Z_{\text{Cl}}Z_{\text{F}}/R \) and \( \varepsilon_0 = E_{\text{Fe}} + |E_{\text{Cl}} + E_{\text{F}}| = -683.1031 \) hartree. Following Bingel \cite{15} the linear term in \( R \) is absent. On the other hand, the behavior of the dissociation energy at large internuclear distances \( R \to \infty \) is

\begin{equation}
E_d = -\frac{C_6}{R^6} + \frac{0}{R^7} + \frac{C_8}{R^8} + \cdots,
\end{equation}

cf. \cite{16}, see Eq.(9) therein, for \( \text{H}_2 \) molecule. Let us emphasize that the term \( 1/R^7 \) is absent. This corresponds to multipole expansion. The van der Waals constant \( C_6 \) for ClF molecule,
to the best of our knowledge, is not known, its value can be estimated as

\[ C_{6}^{(\text{ClF})} = \frac{2 C_{6}^{F} C_{6}^{\text{Cl}}}{\alpha_{F} C_{6}^{F} + \alpha_{\text{Cl}} C_{6}^{\text{Cl}}} , \]

(4)

see [17], where \( \alpha_{F} = 3.74 \text{ a.u.} \) and \( \alpha_{\text{Cl}} = 14.6 \text{ a.u.} \) are the dipole polarizabilities [18] and \( C_{6}^{F} = 9.52 \text{ a.u.} \) and \( C_{6}^{\text{Cl}} = 94.6 \text{ a.u.} \) are the van der Waals constants [19] for the interaction between neutral Fluorine and Chlorine atoms, \( \text{F}_2 \) and \( \text{Cl}_2 \), respectively. After substituting the respective values into (4), the final result for the van der Waals constant is

\[ C_{6}^{(\text{ClF})} \sim 29.3 \text{ a.u.} \]

In order to construct an analytic expression which interpolates the small \( R \) (2) and large \( R \) (3) asymptotic expansions, a rational function in the form of two-point Padé approximant Pade\([N/N + 5](R)\) is proposed [10], so that the potential energy curve is

\[ E_{d}(R) = \frac{1}{R} \text{Pade}[N/N + 5](R)_{n_{0},n_{\infty}} , \]

where \( n_{0} \) is the number of coefficients in the expansion (2) which are reproduced exactly, while \( n_{\infty} \) is the number of coefficients which are reproduced exactly in the expansion at \( R = \infty \) at (3). In concrete calculations we choose \( N = 4 \) and \( n_{0} = 3, n_{\infty} = 2 \). Eventually, we arrive at

\[ E_{d}(R) = \frac{1}{R} \frac{153 + \sum_{i=1}^{3} a_{i} R^{i} - a_{4} R^{4}}{1 + \alpha_{1} R + \alpha_{2} R^{2} + \sum_{i=3}^{7} b_{i} R^{i} - \alpha_{3} R^{8} + b_{9} R^{9}} , \]

(5)

with four constrains imposed

\[
\begin{align*}
\alpha_{1} &= (a_{1} - \varepsilon_{0})/153 , \\
\alpha_{2} &= (\varepsilon_{0}^{2} + 153 a_{2} - a_{1} \varepsilon_{0})/153^{2} , \\
\alpha_{3} &= a_{3}/C_{6} , \\
b_{9} &= a_{4}/C_{6} .
\end{align*}
\]

(6)

These constraints occur in order to guarantee that in the expansions of the two-point Padé approximant (5) at small and large \( R \) the exact coefficients in front of the first three terms \( R^{-1} \), \( R^{0} \) and \( R \) at small internuclear distances (2) and the coefficients in front of the first two terms \( R^{-6} \) and \( R^{-7} \) for large internuclear distances (3) are reproduced. Remaining nine
parameters in (5) are free. These parameters are fixed by choosing nine points among RKR experimental data [4] in domain $R \in [2.6, 3.8]$ bohr to describe them exactly

$$a_1 = -24.4199, \quad b_3 = -5.78426,$$
$$a_2 = -30.0557, \quad b_4 = -2.93344,$$
$$a_3 = 7.75224, \quad b_5 = 4.05190,$$
$$a_4 = 0.70789, \quad b_6 = -2.64498,$$
$$b_7 = 1.16409.$$  

Table I presents the dissociation energy $E_d$ obtained from the analytic expression (5) with parameters (6)-(7) for different internuclear distances $R$, which are compared with the all RKR results from [4]. As can be seen that, except for a few points, not less than 4 decimal digits (d.d.) are in agreement. The function $E_d(R)$ (5) is plotted in Fig. 1 together with the RKR experimental points [4] as well as the numerical theoretical results, extracted from figures in [5] and [6]. It must be emphasized that the results [5] and [6], obtained in different \textit{ab initio} calculations, disagree essentially with each other as well as with RKR experimental data from [4] even though all of them agree in predicting the equilibrium distance $R_{eq}$.

The minimum of the BO potential energy curve $E_d(R)$ is calculated by taking the derivative of (5) $dE_d(R)/R = 0$, obtaining $R_{min} = 3.0781$ bohr and $E_{min} = -0.09797$ hartree in a reasonable agreement with the RKR experimental values $R = 3.0771$ bohr [22] and $E_{min} = -0.09796$ hartree [4]. Note that the dissociation energy vanishes, $E_d(R_0) = 0$, at $R_0 = 2.4671$ bohr.

III. ROVIBRATIONAL SPECTRA

In the Born-Oppenheimer approximation of zero order (when adiabatic correction is neglected), the rovibrational spectra are calculated by solving the nuclear Schrödinger equation

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

where $\mu = m_{Cl}m_F/(m_{Cl} + m_F)$ is the reduced mass for chlorine and fluorine nuclei, $L$ is the angular momentum and $E_{\nu,L}$ is the rovibrational energy of the state with vibrational and rotational quantum numbers $\nu$ and $L$, respectively. The nuclear potential $V(R)$ is the electronic energy given by the two-point Padé approximant (5). Equation (8) is solved
TABLE I: Dissociation energy (in hartree) for the ground state $X^1\Sigma^+$ for the chlorine monofluoride molecule ClF as a function of the internuclear distance $R$. First and second columns are from [4]. The last column is obtained from the approximation (5).

| $R$         | $E_d$ [4] | $E_d$ fit (5) |
|------------|-----------|---------------|
| 2.6743404  | -0.06306  | -0.06299      |
| 2.6900251  | -0.06615  | -0.06615      |
| 2.7068437  | -0.06929  | -0.06933      |
| 2.7249851  | -0.07248  | -0.07252      |
| 2.7450162  | -0.07573  | -0.07577      |
| 2.7671260  | -0.07902  | -0.07904      |
| 2.7922593  | -0.08236  | -0.08237      |
| 2.8211721  | -0.08574  | -0.08572      |
| 2.8561321  | -0.08918  | -0.08914      |
| 2.9012965  | -0.09266  | -0.09262      |
| 2.9714054  | -0.09618  | -0.09615      |
| 3.0771185  | -0.09796  | -0.09797      |
| 3.1955269  | -0.09618  | -0.09621      |
| 3.2915250  | -0.09266  | -0.09267      |
| 3.3625787  | -0.08918  | -0.08918      |
| 3.4238058  | -0.08574  | -0.08574      |
| 3.4793637  | -0.08236  | -0.08234      |
| 3.5313312  | -0.07902  | -0.07900      |
| 3.5806531  | -0.07573  | -0.07571      |
| 3.6282742  | -0.07248  | -0.07247      |
| 3.6745724  | -0.06929  | -0.06928      |
| 3.7197369  | -0.06615  | -0.06615      |
| 3.7641455  | -0.06306  | -0.06308      |

by using the Lagrange Mesh Method [20] (see for code the Appendix). Nuclear masses are
FIG. 1: BO potential energy (in hartree) for the ground state \( X^1\Sigma^+ \) of the ClF molecule vs internuclear distance \( R \): (i) the Padé approximant (5) (red line), (ii) RKR experimental data [4] (red dots) and (iii) points extracted from plots of numerical calculations: 2000 [5] (green triangles) and 2014 [6] (blue diamonds).

The obtained vibrational spectra \( E_{\nu,0} \) is presented in Table II. Comparison with the 10 vibrational states reported in [4] shows a correspondence in 4 d.d. In total there are 48 vibrational states \( (\nu = 0, \ldots, 47) \). However, energies of the states with \( \nu = 45, 46, 47 \) are near the dissociation threshold, they are smaller than \( 10^{-4} \) hartree, thus, beyond our accuracy and have to be excluded.

The complete rovibrational spectra is depicted in the histogram in Figure 2. In total, there are 5719 rovibrational states with \( \nu_{\text{max}} = 47 \) and \( L_{\text{max}} = 210 \), however, as for pure vibrational states \( L = 0 \) the energies of some of them are beyond of our accuracy. Those 5685 rovibrational states obtained with absolute accuracy \( \lesssim 10^{-4} \) hartree with energies \( \lesssim 10^{-4} \) hartree are indicated in blue in the histogram. All these 5719 rovibrational energies are obtained by solving the radial Schrödinger equation (8) with the potential (5) using the Lagrange-Mesh Method [20] in a single run for given \( L \). The code and computational details are presented in Appendix.

chosen as \( m_F = 34622.9705 \) for \(^{19}\text{F} \) and \( m_{\text{Cl}} = 63727.3189 \) for \(^{35}\text{Cl} \) [21].
TABLE II: Vibrational energies $E_{\nu,0}$ in hartree for the ground state $X^1\Sigma^+$ of the ClF molecule. RKR vibrational states [4] for $\nu = 0, \cdots, 10$ are presented in the third column.

| $\nu$ | $E_{\nu,0}$ [4] | $\nu$ | $E_{\nu,0}$ | $\nu$ | $E_{\nu,0}$ | $\nu$ | $E_{\nu,0}$ | $\nu$ | $E_{\nu,0}$ |
|-------|----------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|
| 0     | -0.09619       | 11    | -0.60002    | 21    | -0.03267    | 31    | -0.1209     | 41    | -0.00117    |
| 1     | -0.09266       | 12    | -0.05703    | 22    | -0.03027    | 32    | -0.01050    | 42    | -0.00074    |
| 2     | -0.08918       | 13    | -0.05409    | 23    | -0.02794    | 33    | -0.00901    | 43    | -0.00042    |
| 3     | -0.08574       | 14    | -0.05121    | 24    | -0.02569    | 34    | -0.00762    | 44    | -0.00021    |
| 4     | -0.08235       | 15    | -0.04839    | 25    | -0.02350    | 35    | -0.00635    | 45    | -0.00009    |
| 5     | -0.07901       | 16    | -0.04562    | 26    | -0.02139    | 36    | -0.00518    | 46    | -0.00003    |
| 6     | -0.07572       | 17    | -0.04291    | 27    | -0.01936    | 37    | -0.00414    | 47    | -0.00003    |
| 7     | -0.07248       | 18    | -0.04026    | 28    | -0.01741    | 38    | -0.00321    |
| 8     | -0.06929       | 19    | -0.03766    | 29    | -0.01555    | 39    | -0.00241    |
| 9     | -0.06615       | 20    | -0.03514    | 30    | -0.01377    | 40    | -0.00173    |

As a conclusion we have to state that for the ground state of the diatomic molecule ClF the simple analytic function (5) with parameters (6)-(7) allows to describe the all available RKR experimental data in domain $3.8 > R > 2.7$ bohr with accuracy of four figures and restore the BO potential curve for all internuclear distances. All 5719 rovibrational energies with maximal vibrational number $\nu_{max} = 47$ and maximal angular momentum $L_{max} = 210$ are predicted for the first time. Making an evident modification of the expansions (2) and (3) accordingly an analogue of the function (5) can be written for BO potential curve for the excited states of ClF.

A.V.T. thanks PASPA-UNAM for a support during his sabbatical stay at University of Miami.

[1] A.L. Wahrhaftig, *The Absorption Spectrum of Chlorine Fluoride,*
FIG. 2: Rovibrational spectra for the ground state $X^1\Sigma^+$ of the Chlorine Monofluoride molecule. All rovibrational energies are found with absolute accuracy $\sim 10^{-4}$ hartree. The weakly-bound states of energies $\lesssim 10^{-4}$ hartree are shown in light red.

1. J. Chem. Phys 10, 248 (1942)

2. P.A. Straub and A.D. Mc Lean,
   Electronic Structure of Linear Halogen Compounds,
   Theor. Chem. Acc. 32, 227-242 (1974)

3. K.V. Darvesh, R.J. Boyd and S.D. Peyerimhoff,
   Electronically excited states of chlorine monofluoride: a multireference configuration interaction study,
   J.Chem.Phys 121, 361-369 (1988)

4. I.S. McDermid,
   Potential-energy Curves, Franck-Condon Factors and Laser Excitation Spectrum for the $B^3\Pi(0^+)-X^1\Sigma^+$ System of Chlorine Monofluoride,
   J.Chem.Soc., Faraday Trans. 77, 519-530 (1981)

5. A.B. Alekseyev, H.-P. Liebermann, R.J. Buenker and D.B. Kokh,
   Relativistic configuration interaction study of the ClF molecule and its emission spectra from $^+\text{ion-pair states}$,
J. Chem. Phys. 112, 2274-2288 (2000)

[6] A.A. Vassilakis, A. Kalemos and A. Mavridis,

Accurate first principles calculations on chlorine fluoride ClF and its ions ClF⁺,

Theor. Chem. Acc. 133:1436, 1-15 (2014)

[7] M. Diegelmann, K. Hohla, F. Rebentrost, and K.L. Kompa

Diatomic interhalogen laser molecules: Fluorescence spectroscopy and reaction kinetics,

J. Chem. Phys. 76, 1233-1247 (1982)

[8] M. Diegelmann, D. Proch and Z. Zhensheng

Discharge Pumped ClF Laser at 285 nm,

Appl. Phys. B 40, 49-58 (1986)

[9] N. N. Greenwood and A. Earnshaw,

Chemistry of the elements,

2nd edn. Butterworth-Heinemann, Oxford (1998)

[10] A.V. Turbiner and H. Olivares Pilón, Towards the analytic theory of Potential Energy Curves for diatomic molecules. Studying He₂⁺ and LiH dimers as illustration,

Mol. Phys. e2064784 (2022) (invited contribution to L. Wolniewicz Special Issue),

DOI: 10.1080/00268976.2022.2064784

[11] H. Olivares-Pilón and A.V. Turbiner,

The H₂⁺ molecular ion: low-lying states,

Ann. Phys. 373, 581-608 (2016)

[12] H. Olivares-Pilón and A.V. Turbiner,

H₂⁺, HeH and H₂: Approximating potential curves, calculating rovibrational states,

Ann. Phys. 393, 335-357 (2018); ibid 408, 51 (2019) (erratum)

[13] A.V. Turbiner, J.C. Lopez Vieyra and H. Olivares Pilón,

Few-electron atomic ions in non-relativistic QED: Ground state energy,

Ann. Phys. 409 (2019) 167908 (19 pp)

[14] S. J. Chakravorty, S. R. Gwaltney and E R. Davidson,

Ground-state correlation energies for atomic ions with 3 to 18 electrons,

Phys. Rev. A 47, 3649 - 3670 (1993)

[15] W. A. Bingel,

United atom treatment of the behavior of potential energy curves of diatomic molecules for
small $R$,

*J. Chem. Phys* 30, 1250-1253 (1958)

[16] L. Pauling and J.Y. Beach,

*The van der Waals Interaction of Hydrogen Atoms*,

*Phys. Rev.* 47, 686 - 692 (1935)

[17] K. T. Tang,

*Dynamic Polarizabilities and van der Waals Coefficients*,

*Phys. Rev.* 177, 108 - 114 (1969)

[18] P. Schwerdtfegera and J. K. Nagleb,

*2018 Table of static dipole polarizabilities of the neutral elements in the periodic table*,

*Mol. Phys* 117, 1200–1225 (2019)

[19] X. Chu and A. Dalgarno,

*Linear response time-dependent density functional theory for van der Waals coefficients*,

*J. Chem. Phys* 121, 4083-4088 (2004)

[20] D. Baye,

*The Lagrange-mesh method*,

*Phys. Rep* 565, 1-107 (2015)

[21] G. Audi, A. H. Wapstra and C. Thibault,

*The AME2003 atomic mass evaluation*,

*Nucl. Phys. A* 729, 337-676 (2003)

[22] R. E. Jr Willis, and W. W. Clark,

*Millimeter wave measurements of the rotational spectra of CIF, BrF, BrCl, ICl, and IBr*,

*J. Chem. Phys.* 72, 4946-4950 (1980)
Appendix

The code based on the Lagrange Mesh Method written in Mathematica-12 is shown by taking the zero angular momentum (vibrational states) as the example. Mesh points correspond to the zeroes of the Laguerre polynomials. Number of used mesh points varies from 400 for small $L$ to 800 for largest angular momentum $L$ denoted as $ll$. Scaling parameter $\hbar$, see [20], used to accelerate convergence, varies for 0.04 to 0.5 depending on the angular momentum $L$. For given $L$ the rovibrational spectra is found in a single run. It takes $\sim 10^2$ seconds of CPU time on a standard laptop. For confidence the obtained results were recalculated using the code written in FORTRAN-90.
n = 400;
l = 0;
h = 0.04;

solsxx = NSolve[Laguerre[n, x] == 0, x, WorkingPrecision -> 10];
k = 0;
solsxx /. 
{r___Rule} :> Set @@ ( {r} /. x -> Subscript[var, ++k]);

Kinetic T

Tx0[x_, y_] = 
(Sqrt[x + y*(x - y)^2])

Do[For[i = 1, j < i, j++, 
Tx[i, j] = (-1)^(i - j) * Tx0[x1, x1]; 
Tx[j, i] = Tx[i, j], 
{i, 1, n}];

Do[Tx[i, i] = 
1/12 * x_i^2 * (x_i^2 - 2 * (2 * n + 1) * x_i - 4), 
{i, 1, n}];

Potential V

eF = -1242.985;
eF = -99.7339;
eC = -460.148;
Z = 9;
Z = 17;
Z = ZF + ZCl;
c = 29.3;
eI = eF + eCl;
eI = (eFe + Abs[eI]);
a1 = -24.4199;
a2 = -30.0557;
a3 = 7.75224;
a4 = 0.78789;
b3 = -5.78426;
b4 = -2.93344;
b5 = 4.05190;
b6 = -2.64498;
b7 = 1.16409;
b9 = a4/c6;

xmF = 34622.970483879;
xmCl = 63727.31892234;
xMn = xMn * xMCl / (xmF * xMCl);

VV[x_] := 
(ll *(ll + 1)) / 2 * xMn * x^2 + 
(ZZ * a1 * x + a2 * x^2 + a3 * x^3 + a4 * x^4) / 
(x * (1 + (a1 - e0)) / ZZ + x * (e0^2 * a2 * ZZ - a1 * e0) / ZZ^2 * x^2 + 
b3 * x^3 + b4 * x^4 + b5 * x^5 + b6 * x^6 + b7 * x^7 - a3 / c6 * x^8 + b9 * x^9));

Hamiltonian

k1 = 0;

Do[k1++;

HHT[i, j] = 
Tx[i, j] / 2 * xMn * h^4

MH = Table[HHT[i, j], 
{i, 1, n}, 
{j, 1, n}];

egv = Eigenvalues[MH]