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Relativistic calculations of the potential energy curve and QED-corrections for the ground state of the CO molecule

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A non-empirical relativistic calculation of the potential energy curve of the ground $X^1\Sigma^+$ state of the carbon monoxide (CO) molecule in the internuclear distances range $R_{AB} \in [0.5, 30.0]$ a.u. is performed. The calculation is carried out by the multireference configuration-interaction method in the basis of the Dirac-Fock-Sturm orbitals. For the entire specified range of distances, multi-electron quantum-electrodynamic corrections to the CO energy are calculated by the method of the model Lamb shift operator. The contributions of the quantum electrodynamic corrections to the value of the equilibrium internuclear distance R^e_{AB}, the dissociation energy D_e and the vibrational constant ω_e of the CO molecule are obtained.

Keywords: relativistic effects, correlation effects, quantum-electrodynamics corrections, carbon monoxide.

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1. Introduction

As one of the most widespread molecules in the universe [1–3], carbon monoxide (CO) is an important object of study in modern physics and astrophysics. Accurate spectroscopic data on the CO molecule make it possible to study the isotopic composition of the Sun [4], the history and development of the Solar System [5], galactic structures and star formation [6]. The CO molecule plays an important role in the chemistry of the atmosphere of Mars [7], Venus [8], as well as gas giant exoplanets [9]. In addition, carbon monoxide (a gas made from CO molecules) is an essential component of the earth's atmosphere, because chemical reactions with it form CO_2 and O_3 pollutants, which are greenhouse gases [10–13] and negatively affect human health [14]. Studying the concentration of CO in different regions of the planet allows monitoring the dynamic processes in the earth's atmosphere [15]. The analysis of many experimental results and observations requires theoretical data on the spectroscopic parameters of the CO molecule.

One of the important spectroscopic characteristics of a molecule is the potential energy curve. It can be used to calculate vibrational frequencies, equilibrium internuclear distance, dissociation energy and other properties of the molecule. Theoretical studies of potential energy curves for low-lying CO states have been performed by many research groups. In [16–22] various semi-empirical methods were used. Some sections of the potential energy curve of the CO molecule were calculated by *ab initio* methods [22–26]. However, the need to calculate the potential energy curve of the CO molecule using a single *ab initio* method remains urgent in a wide range of internuclear distances both in the region of the potential minimum and in the region of the dissociation limit.

To compare the results of high-precision theoretical calculations with experimental data, especially for molecules containing heavy atoms, it may be necessary to take into account quantum electrodynamic (QED) contributions to the electronic energy of the molecule. Rigorous *ab initio* calculation of QED-corrections in multielectron atoms and, especially, in multielectron molecules is a very complex and time-consuming task. Previously, *ab initio* calculations of QED-corrections were carried out only for one-electron quasi-molecules containing heavy nuclei [27,28] and the simplest light molecules H_2, HD, H_2^+ [29]. In [30], the model operator method [31] was used to calculate QED-corrections in one-electron quasi-molecules. Some modification of this method was used in calculations of heavy molecules [32,33]. In [34,35], to take into account the QED-corrections in molecules, the model radiative operator proposed earlier in [36] was used. The contribution of the Lamb shift to the energy of the ground state of the CO molecule at an equilibrium distance was assessed in [25] using a semi-empirical method.

The first attempts to use the basis of non-relativistic Sturmian functions in calculations of the electronic structure of atoms were made by M. Rotenberg [37]. The application of the basis of Sturmian functions in calculations of atoms using the non-relativistic Hartree-Fock method is presented in [38]. The use of the multireference configuration-interaction method in the Dirac-Fock-Sturm orbital basis (MRCI-DFS) in relativistic calculations of atoms is described in our study [39], see also [40,41]. One of the main objectives of this study was the development of the relativistic MRCI-DFS method for calculating the potential energy of diatomic molecules. In this study, this method was used to calculate the potential energy curve of the ground state $X^1\Sigma^+$ of the CO molecule in the region of internuclear distances of 0.5−30.0 a.u.

Another task was to develop a method for calculating QED-corrections to the electronic energy of multielectron diatomic molecules, based on the use of a model QED operator. For a description of this model operator and its application in calculations of QED-corrections in multielectron atoms and ions, see [31,42–44]. Earlier in [30], the model operator method was applied in the calculations of QED-corrections in one-electron diatomic quasi-molecules. In this study, the scope of application of the model QED operator is extended to multielectron diatomic molecules. Using the model QED operator method, we calculated QED-corrections to the energy of the ground state of the CO molecule in the region of internuclear distances of 0.5−30.0 a.u. In addition, the contribution of QED-corrections to the equilibrium internuclear distance R^e_{AB}, dissociation energy D_e and vibrational constant ω_e of the CO molecule was calculated.

This study is structured as follows. The second section describes the theoretical methods used in this study. The third section presents the results obtained, their discussion and comparison with literature data.

By default, the study uses the atomic system of units ($e = m = \hbar = 1$), unless otherwise specified.

2. Theoretical methods

Calculations of the energy of a CO molecule as a function of the internuclear distance in this study were performed in the Born-Oppenheimer approximation. To solve the molecular many-electron Dirac equation, the MRCI-DFS method was used. The Dirac-Coulomb (DC) Hamiltonian was taken as the Hamiltonian of the molecular system:

$$\hat{H}_{\mathrm{DC}} = \Lambda^{(+)} \left[\hat{H}_{\mathrm{D}} + \hat{V}_{\mathrm{C}}\right] \Lambda^{(+)}. \tag{1}$$

Here $\hat{H}_{\mathrm{D}}$ is the sum of the one-electron Dirac Hamiltonians

$$\hat{H}_{\mathrm{D}} = \sum_{i}^{N} \hat{h}_{\mathrm{D}}(i), \tag{2}$$

where

$$\hat{h}_{\mathrm{D}} = c(\boldsymbol{\alpha} \cdot \boldsymbol{p}) + mc^2(\beta - 1) + V_{AB}(\boldsymbol{r}), \tag{3}$$

$\boldsymbol{p}$ is the momentum operator, $\boldsymbol{\alpha}$ and β are the Dirac matrices, V_{AB} is the potential created by nuclei:

$$V_{AB}(\boldsymbol{r}) = V^{A}_{\mathrm{nucl}}(\boldsymbol{r} - \boldsymbol{R}_A) + V^{B}_{\mathrm{nucl}}(\boldsymbol{r} - \boldsymbol{R}_B), \tag{4}$$

$\boldsymbol{R}_A$, $\boldsymbol{R}_B$ are the radius vectors of nuclei A and B, respectively. When building up the nuclear potentials $V^{A,B}_{\mathrm{nucl}}(\boldsymbol{r})$, the finite size of the nucleus was taken into account. The values of the root-mean-square radii of carbon and oxygen nuclei were taken from [45]. The interelectronic interaction operator $\hat{V}_{\mathrm{C}}$ in equation (1) is determined as follows

$$\hat{V}_{\mathrm{C}} = \frac{1}{2}\sum_{i \neq j}^{N} \frac{1}{r_{ij}}, \quad r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|. \tag{5}$$

The projectors $\Lambda^{(+)}$ in Hamiltonian (1) are the direct product of the one-electron projectors and the positive spectrum of the Dirac-Fock (DF) operator. In this study, the Breit interaction is omitted. It can be taken into account separately [25].

The multielectron wave function Ψ_Ω with a certain value of the projection Ω of the total angular momentum onto the internuclear axis is represented as a linear combination of Slater determinants built up on one-electron molecular orbitals

$$\Psi_\Omega = \sum_{\beta} C_\beta(\Omega)\mathrm{det}_\beta(\Omega). \tag{6}$$

In the case of closed shells, as is the case for the ground state of the CO molecule, the projection is $\Omega = 0$. For each internuclear distance $R_{AB} = |\boldsymbol{R}_A - \boldsymbol{R}_B|$, the problem of determining the coefficients $C_\beta(\Omega)$ is reduced to an eigenproblem

$$H_{\mathrm{DC}}\mathbf{C}(\Omega) = E_{\mathrm{DC}}(\Omega)\mathbf{C}(\Omega), \tag{7}$$

where H_{DC} is matrix of the DC Hamiltonian in the Slater determinant basis, $\mathbf{C}(\Omega)$ is column vector consisting of expansion coefficients (6).

Molecular orbitals $\psi_i(\boldsymbol{r})$ are expanded in a two-center basis of DFS orbitals centered at points A and B

$$\psi_i(\boldsymbol{r}) = \sum_{\alpha=A,B} \sum_{a} u^{i}_{\alpha,a}\phi_{\alpha,a}(\boldsymbol{r} - \boldsymbol{R}_\alpha). \tag{8}$$

The DFS basis functions $\phi_{\alpha,a}(\boldsymbol{r} - \boldsymbol{R}_\alpha)$ are central field Dirac bispinors centered on nuclei A and B. The subscript $a = n, \kappa, m$ represents the quantum numbers of the basis functions, n is principal quantum number, κ is Dirac angular quantum number, m is angular momentum projection. The expansion coefficients $u^{i}_{\alpha,a}$ of molecular orbitals $\psi_i(\mathbf{r})$ over the DFS basis are solutions to the two-center DF equations in matrix form

$$F\boldsymbol{U}_i = \varepsilon_i S\boldsymbol{U}_i, \tag{9}$$

where F is standard Fock matrix in the restricted DF method in the basis of the one-electron DFS functions, S is the non-orthogonality matrix (matrix of overlap integrals), $\boldsymbol{U}_i$ is column vector of expansion coefficients (8).

The basis of the one-electron DFS functions is constructed as follows. The orbitals of occupied and partially occupied states $1s$, $2s$, and $2p$ of C and O atoms are determined by numerically solving the integro-differential DF equations [46]. Virtual orbitals are Sturmian functions, which are numerical solutions to the so-called Dirac-Fock-Sturm equation

$$(\hat{h}^{\mathrm{DF}} - \varepsilon_0)\phi_j = \lambda_j W(r)\phi_j, \tag{10}$$

where $\hat{h}^{\mathrm{DF}}$ is DF operator, ε_0 is reference energy, which is the energy of DF orbitals ns, np or nd, $W(r)$ is weight function of the following form

$$W(r) = \left[\frac{1 - e^{-(ar)^2}}{(ar)^2}\right]^n. \tag{11}$$

The parameters a and n are selected in a certain way in order to achieve the fastest convergence of the energy $E_{\mathrm{DC}}(\Omega)$ in terms of the number of virtual orbitals. The relativistic DFS equation is described in more detail in [39–41,47].

To implement the CI-DFS method for diatomic molecules, it is necessary to calculate one-electron and two-electron two-center matrix elements with the DFS basis functions numerically specified on the radial grid. In this study, the calculation of two-center matrix elements with such functions is based on the use of a symmetric expansion [47–49] of the product of two orbitals of different centers. This symmetric expansion is a modification of Lewdin's re-expansion [50] of the atomic orbitals of one center to another. The procedure for calculating one-electron relativistic matrix elements of the Dirac operator was described in detail earlier [47]. Expressions for two-electron two-center matrix elements are much more cumbersome. Some of them are described in [51].

Calculations of QED-corrections to the electronic energy of the ground state of the CO molecule were performed using a model QED operator, which is described in [30,31,42–44]. The model QED operator is constructed in such a way as to reproduce the exact values of the matrix elements of single-loop QED contributions for low-lying states of hydrogen-like ions. In calculations of QED-corrections to the energy of the CO molecule, the finite field method was used, i. e. the model operator was added to the Dirac-Coulomb Hamiltonians (1) and DF ($\hat{h}^{\mathrm{DF}}$). In addition, the matrix elements of the model operator were added to the Fock matrix F. Thus, QED contributions were taken into account when building up the DFS basis, when solving the molecular DF equations (9), as well as when calculating the matrix H_{DC}. The QED-correction to energy was defined as the difference between the total electronic energy of a molecule with and without the inclusion of a model operator.

3. Calculation results

For the ground state of the $^{12}C^{16}O$ molecule, calculations of the potential energy curve were performed in the Born-Oppeheimer approximation in the interatomic distance range of $0.5-30.0$ a.u. When building up the configuration space, all possible single and double excitations from several reference configurations into the spaces of active and virtual orbitals were considered. In this study, the DFS functions with the principal quantum number $n \leq 5$ and the orbital quantum number $l \leq 3$ were used as a one-electron basis set at each center, and $6s$-orbital DFS was additionally added. The lowest molecular orbitals formed by the $1s$ orbitals of each atom were included in the frozen core and thereby excluded from the active space.

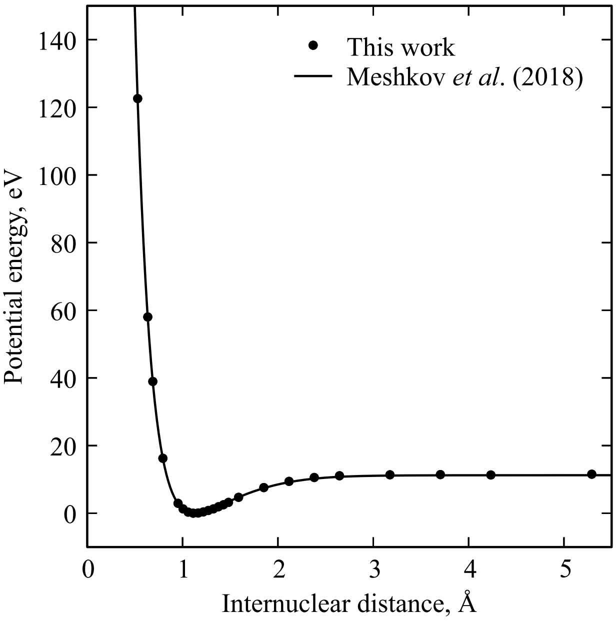

Figure 1. Dependence of the potential energy of the ground state $X^1\Sigma^+$ of the CO molecule as a function of the internuclear distance, calculated by the CI-DFS method, as well as comparison with the semi-empirical curve from [22].

Fig. 1 and 2 show the results of calculations of the potential energy curve of the CO molecule obtained in this study (thick dots) and the semi-empirical potential energy curve (solid line) taken from [22]. Fig. 1 presents the results obtained in a wide range of distances $R_{AB} \in [0.5, 5.5]$ Å, and Fig. 2 shows in more detail the region of minimum of the potential curve. The analytic curve approximating experimental data and *ab initio* calculations obtained in [22] has a correct behavior in a wide range of interatomic distances and, in particular, at $R_{AB} \to 0$ and in the dissociation limit. Comparison of the results of our calculations with the semi-empirical data presented in Fig. 1 and 2 shows that the points of the potential energy curve obtained in this study are in good agreement with the semi-empirical curve [22].

Further, the QED-corrections to the total energy of the CO molecule were calculated. When calculating QED-corrections, $3s$, $3p$ functions for each atom were used as atomic virtual orbitals. Fig. 3 shows a graph of the magnitude of the QED-corrections as a function of the internuclear distance. It can be seen from Fig. 3 that the depth of the minimum of the QED-correction curve is of the order of $3\,\mathrm{cm}^{-1}$.

Using the potential energy curve obtained in this study, the equilibrium internuclear distance R^{e}_{AB}, the dissociation energy D_{e}, and the vibrational constant ω_e of the CO molecule were calculated. In addition, the contributions of QED-corrections to the above-listed spectroscopic constants were calculated. The values of R^{e}_{AB} and ω_{e} were determined

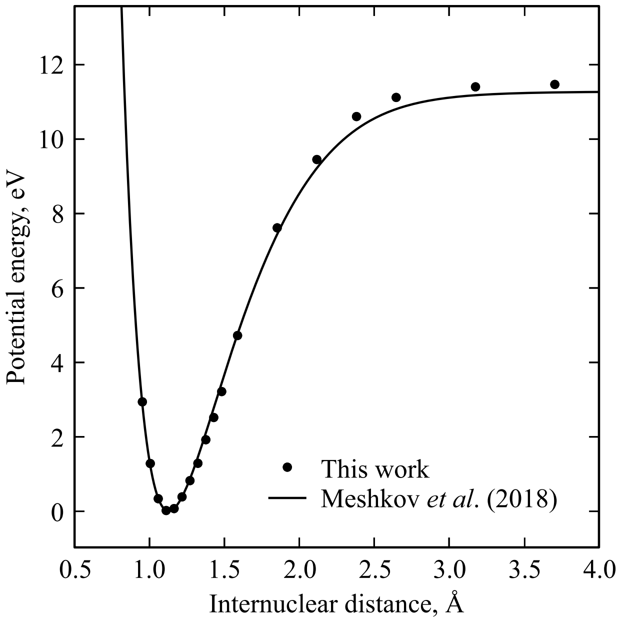

Figure 2. Dependence of the potential energy of the ground state $X^1\Sigma^+$ of the CO molecule as a function of the internuclear distance, calculated by the CI-DFS method, as well as comparison with the semi-empirical curve from [22].

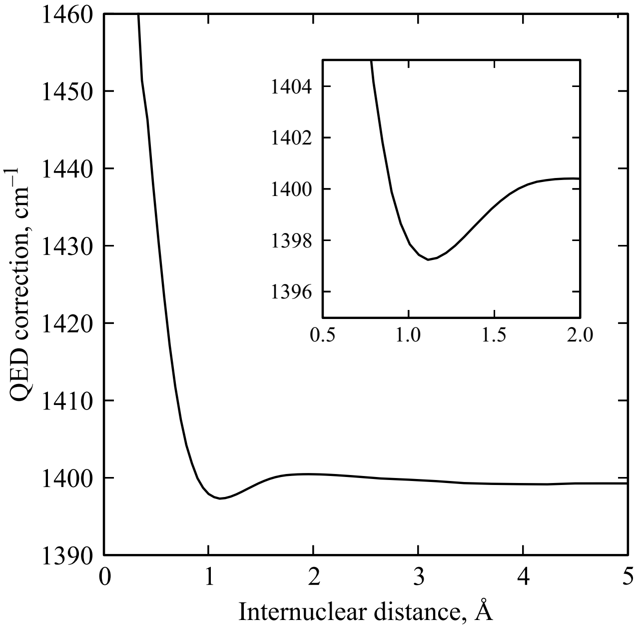

Figure 3. Dependence of QED-corrections to the potential energy of the ground state $X^1\Sigma^+$ of the CO molecule on the internuclear distance, calculated using the model QED operator method.

using the OpenMolcas software package. The dissociation energy D_e was obtained as the difference between the total energy of CO at a distance of 30 a.u. and the energy at the minimum of the potential curve.

The table shows values of R^e_{AB}, D_e and ω_e obtained in this study, taking into account QED-corrections (3-rd column) and without taking into account QED-corrections (2-nd column). A comparison is given with the results of [19] presented in the 4-th column of the table. The values of R^e_{AB}, D_e were determined using the semi-empirical potential W_{BO} [19]. The ω_e constant was obtained as double the value of G_0 from [19].

Results of calculation of the equilibrium interatomic distance R^e_{AB} (Å), dissociation energy D_e (cm^{-1}), and vibrational constant ω_e (cm $^{-1}$) and comparison with the data of [19]

Parameter	DC	DC + QED	[19]
R^e_{AB} (Å)	1.1284	1.1284	1.1282
D_e (cm^{-1})	88066	88068	90674
ω_e (cm^{-1})	2104.4	2104.5	2163.6

As can be seen from the table, taking into account the QED-correction has virtually no effect on the value of the equilibrium distance. Indeed, the value of R^e_{AB}, calculated both without and with QED-corrections, is 1.1284 Å. This value agrees well with the equilibrium distance 1.1282 Å obtained in [19]. The dissociation energy D_e, calculated using the DC Hamiltonian, is equal to 88066 cm^{-1}. The value of the QED-correction to the dissociation energy calculated by us is of the order of 3 cm^{-1}, which can be compared with the estimate of 3−4 cm^{-1} obtained in [25] by semi-empirical scaling of the one-electron Darwin term. The difference between our value of D_e and the result of [19] is approximately 3%. The value of the vibrational constant ω_e, obtained without taking into account QED-corrections, is 2104.4 cm^{-1}. The inclusion of the model QED operator in the calculation introduces a very small correction to this value of the order of 0.1 cm^{-1}. The difference between the value of ω_e in this study and the value from [19] is at the level of 3%.

Of course, the values of QED-corrections for the CO molecule are negligible compared to the error in the values of the spectroscopic constants we obtained. However, the values of QED-corrections may be of independent interest and can be taken into account when comparing the results of more accurate calculations with experimental data. In addition, the method we developed for calculating QED contributions to the spectral characteristics of diatomic molecules can be useful in calculating the electronic structure of molecules containing heavier atoms.

4. Conclusion

In this study, the potential energy curve of the CO molecule is calculated for internuclear distances $R_{AB} \in [0.5, 30.0]$ a.u. by the method of configuration interaction in the basis of Dirac-Fock-Sturm orbitals. For these distances, multielectron QED-corrections were also calculated using the method of model QED operator. In addition, the equilibrium internuclear distance R^e_{AB}, the dissociation energy D_e, and the vibrational constant ω_e of the CO molecule were calculated taking into account QED-corrections. Comparison of the resulting potential energy curve, as well as the molecular constants, with the data from previous studies shows reasonable agreement of the results.

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Conflict of interest

The authors declare that they have no conflict of interest.

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