Semiempirical dipole moment functions of the CO and NO molecules

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A semiempirical method has been developed for calculation of the dipole moment functions for the NO and CO molecules in the piecewise-continuous form. The dipole moment functions obtained exhibit a physically correct asymptotic behavior at small and large internuclear separations and agree with the dipole moment functions near the nuclear equilibrium position of the molecule. Within the framework of this approach, the account for the multipole and exchange interactions allows us to improve the dipole moment functions at large internuclear separations, including the range of slight overlapping of electron shells of the interacting atoms.

Introduction

The carbon monoxide, CO, and nitrogen monoxide, NO, molecules are among the most stable diatomic molecules in the Earth's atmosphere. These molecules were also found in the interstellar space and other planetary atmospheres. Although the carbon and nitrogen monoxides are minor constituents of the Earth's atmosphere, their role in atmospheric physical and chemical processes is quite significant. Various physical properties of these molecules have been studied in numerous papers, but some their characteristics, in particular, dipole moment functions still call for further investigation. The concept of the dipole moment function of a diatomic molecule arises due to application of the adiabatic approximation. In this approximation, the dipole moment of a molecule becomes a function of its internuclear separation R, which is a more complete and important characteristic of a molecule that the dipole moment in the equilibrium state R_e that is usually given in the reference literature.

The scientific literature discusses various approaches and methods to construct the dipole moment functions of the CO and NO molecules. One group incorporates methods for description of the dipole moment functions in a limited variability range of internuclear separations of these molecules, for example, near their equilibrium positions. It includes both *ab initio* calculations of the dipole moment functions[1–7] and dipole moment functions near the equilibrium position specified as a Taylor series, whose coefficients are determined from intensities of the absorption lines.[8–11] Another group incorporates semi-empiric methods, for example, Pade approximation[12–14] and the exponential forms,[15,16] which allow one to describe the dipole moment functions all over the range of internuclear separations of the CO and NO molecules. Though the

dipole moment functions specified by the Pade approximation or exponential forms may be close to real ones, they fail to describe the physical pattern of formation of the dipole moment function of molecules because no physically justified criteria for selection of these forms exist.

In this paper we propose different approach to construction of the dipole moment functions of the CO and NO molecules for the whole range of their internuclear separations. Within the proposed method, the dipole moments of the molecules are represented by piecewise-continuous functions exhibiting physically correct asymptotic behavior at small and large internuclear separations and coinciding with the experimental dipole moment functions near the equilibrium position of the nuclei.

Asymptotic description of the dipole moment functions

Determination of a dipole moment function of a molecule is a complicated problem that requires calculation of the wave function of a molecule for arbitrary values of its internuclear separations R. There are three subranges of internuclear separations, in which the wave function can be specified analytically: subrange of small R values and subrange of large R values, which, in its turn, can be divided into two parts depending on the type of dominating interaction: multipole (at $R \to \infty$) and exchange (at smaller R) interactions.

Subrange of small R

For small internuclear separations ($R \to 0$) the molecular wave function can be calculated by methods of the perturbation theory with the wave functions of the "joint" atom taken as zero-approximation functions. So in the first order of the

perturbation theory approximation the dipole moment function of the molecule in the ground electronic state can be represented as

$$\mu(R) = 2\sum_m \frac{V_{0m}(R)\mu_{m0}}{E_0 - E_m}, \qquad (1)$$

where E_k is the energy of the kth state of the joint atom; μ_{m0} are matrix elements of the dipole moment operator, and the matrix elements of the perturbation operator $V_{0m}(R)$ have the form[17]:

$$V_{0m}(R) = A_{0m} R^3 + B_{0m} R^4 + C_{0m} R^5 + \dots . \qquad (2)$$

As a result, the dipole moment function in the subrange of small R can be written as

$$\mu(R) = \sum_{i=3} a_i R^i, \qquad (3)$$

where the coefficients a_i are individual for every molecule.

Subrange of multipole interaction

In this subrange of the internuclear separations, the molecular wave function can also be calculated by the methods of perturbation theory, but now the products of the wave functions of atoms forming the molecule can be taken as zero-approximation functions. In this case, the dipole moment function of the molecule can be expressed through the characteristics of individual atoms, just which do determine its asymptotic behavior at $R \to \infty$.

If at $R \to \infty$ the molecule XY decomposes into the atoms X and Y having quadrupole moments, then the decisive contribution to the dipole moment functions of the molecule XY is due to the dipole-quadrupole interaction operator

$$\hat{V}(R) = \frac{3}{R^4}\left(\hat{\mu}_z^X \hat{Q}_{zz}^Y - \hat{\mu}_z^Y \hat{Q}_{zz}^X\right), \qquad (4)$$

where $\hat{\mu}_z^X$ is the z-component of the dipole moment operator of the atom X (the axis z coincides with the molecular axis); the zz-component of the quadrupole moment operator of the atom Y has the form

$$\hat{Q}_{zz}^Y = \frac{e}{2}\sum_i (3z_i^2 - r_i^2). \qquad (5)$$

As a result, the dipole moment function of the molecule can be written in the form

$$\mu^{XY}(R) = \frac{C(L^X, M_L^X, L^Y, M_L^Y)}{R^4}, \qquad (6)$$

where

$$C\left(L^X, M_L^X, L^Y, M_L^Y\right) = 3[\alpha_{zz}^X(L^X, M_L^X)Q_{zz}^Y(L^Y, M_L^Y) -$$
$$-\alpha_{zz}^Y(L^Y, M_L^Y)Q_{zz}^X(L^X, M_L^X)],$$

and $\alpha_{zz}^X\left(L^X, M_L^X\right)$ and $Q_{zz}^X\left(L^X, M_L^X\right)$ are the static polarizability and the quadrupole moment of the atom

X in the state with a preset values of the orbital moment quantum numbers L and M_L. In this case, for the values M_L^X and M_L^Y the following condition $\left|M_L^X + M_L^Y\right| = \Lambda$ (Λ is the projection of the orbital angular momentum of electrons onto the molecular axis) is fulfilled. Fulfillment of this condition in the general case can lead to several decomposition channels for the molecule that correspond to different states M_L of the atoms X and Y. This results in different dipole moment functions of the molecule $\mu^{XY}(R)$ for different decomposition channels.

Subrange of the exchange interaction

This subrange of internuclear separations is characterized by slight overlap of the electron shells of the interacting atoms, which results in the exchange of valence electrons. To find the wave function of these electrons, it is possible to use asymptotic methods.[18] The two-electron molecular wave function in this case can be written as

$$\Psi = c_1\psi_1 + c_2\psi_2, \qquad (8)$$

where

$$\psi_1 = \varphi_X(1)\varphi_Y(2)\chi_1, \quad \psi_2 = \varphi_X(2)\varphi_Y(1)\chi_2. \qquad (9)$$

In Eq. (9) $\varphi_X(1)$, $\varphi_Y(1)$ and $\varphi_X(2)$, $\varphi_Y(2)$ are asymptotic coordinate wave functions of the first and second electrons located largely near the atomic cores X and Y. The explicit forms of the functions χ_1 and χ_2 with regard for the interaction of the electrons with each other and with foreign nuclei can be found in Ref. 18.

The contribution of the exchange interaction to the dipole moment function (in a. u.) obtained by averaging the dipole moment operator with function (8) can be presented in the form

$$\tilde{\mu}(R) = B(R)R^\delta \exp[-R(\beta^X + \beta^Y)], \qquad (10)$$

where $B(R)$ is the function weakly depending on R for the subrange of internuclear separations considered; $(\beta^X)^2/2$ and $(\beta^Y)^2/2$ are the ionization potentials of the atoms X and Y, and

$$\delta = 2/\beta^X + 2/\beta^Y - 2/(\beta^X + \beta^Y) + 1. \qquad (11)$$

Note that the multipole interactions also contribute to the dipole moment function in this subrange.

Model of the dipole moment function

The dipole moment function of a diatomic molecule is modeled as a piecewise-continuous function consisting of three parts: dipole moment function in the subrange of small R in the form of polynomial (3), dipole moment function in the subrange of large R [Eqs. (6) and (10)], as well as dipole moment function in the intermediate subrange

$$\mu(R) = \begin{cases} \sum_{i=3} a_i R^i, & 0 \leq R \leq R_1, \\ \sum_{i=0}^{5} b_i R^i, & R_1 \leq R \leq R_2, \\ B_0 R^\delta \exp\left[-R(\beta^X + \beta^Y)\right] + \mu^{XY}(R), & R \geq R_2. \end{cases}$$

$$(12)$$

In this model, the coefficients a_i are determined using known values of the dipole moment function and its derivatives at the equilibrium internuclear separation in the molecule R_e. As a result, the coefficients a_i become some effective parameters, and they are the solution of a system of linear equations, which is found from the condition that the derivatives of the dipole moment function (3) at the point R_e are equal to the derivatives of the dipole moment function in the vicinity of the equilibrium position of the molecule's nuclei

$$\mu(R) = \sum_{i=0} M_i x^i, \qquad (13)$$

where $x = (R - R_e)/R_e$; M_i are experimentally determined coefficients. The coefficients a_i calculated in such a way allow the dipole moment function of the molecule to be specified in the range of small R, including the vicinity of the equilibrium internuclear separation. The number of coefficients a_i is determined by the number of known coefficients M_i.

The dipole moment function in the range of large R can be represented as a sum of the multipole and exchange parts specified by Eqs. (6) and (10), where $B(R)$ is considered as an effective parameter B_0, whose value can be determined by fitting to the data of *ab initio* calculations. This form of the dipole moment function is a good approximation for the range of internuclear separations, where the electron shells of the interacting atoms overlap only slightly.

The dipole moment function in the intermediate range of internuclear separations is a lacing function and is specified by the five-order polynomial with respect to R. The coefficients of this polynomial b_i are determined from the conditions of lacing the dipole moment functions at small and large R accurate to the second derivatives inclusive. Joining points in this work are chosen as follows: $R_1 \approx 1.1 R_e$ and $R_2 \approx 2 R_e$. Selection of the joining points can be done with some arbitrariness, which does not significantly change the form of the dipole moment function.

Calculation of the dipole moment functions of the CO and NO molecules

According to the rules of electron terms correlation of a molecule and the atoms, into which the molecule decompose at $R \to \infty$, the CO molecule in the ground electronic state $^1\Sigma^+$ decomposes into the atom C in the state $^2P(M_L = 0, \pm 1)$ and the atom O in the state $^3P(M_L = 0, \pm 1)$, while the NO molecule in the ground electronic state $^2\Pi$ decomposes into the atom N in the state $^4S(M_L = 0)$ and the atom O in the state $^3P(M_L = \pm 1)$. It follows herefrom that three decomposition channels are possible for the CO molecule, and two channels are possible for NO. In this connection, to find the parameter B_0 by fitting of dipole moment function (12) in the range $R \geq R_2$ to the data of *ab initio* calculations, it is necessary to use the dipole moment function averaged over the decomposition channels

$$\mu^{XY}(R) = \bar{C}^{XY}/R^4, \qquad (14)$$

where

$$\bar{C}^{CO} = \frac{1}{3}\left[C(1,0,1,0) + C(1,1,1,-1) + C(1,-1,1,1)\right],$$

$$\bar{C}^{NO} = \frac{1}{2}\left[C(0,0,1,-1) + C(0,0,1,1)\right]. \qquad (15)$$

The model proposed above was used to construct the dipole moment functions of the CO and NO molecules averaged over their decomposition channels. The atomic parameters used in the calculation of the dipole moment functions are summarized in Table 1. Table 2 presents the values of M_i and the coefficients a_i calculated using them along with the parameters of the polynomials b_i, the coefficients B_0 and $\bar{C}$, as well as lacing points R_1 and R_2. For the CO molecule the parameter B_0 was determined by the least-squares method from the data of *ab initio* calculations of the dipole moment function for $R = 2.28$, 2.38, and 2.65 Å [Ref. 2]. For the NO molecule the available results of *ab initio* calculations of the dipole moment functions[6,7] differ considerably. For this reason, in determining the parameter B_0 for the NO molecule, we took the *ab initio* values of the dipole moment functions from Ref. 7 for $R = 1.74$, 1.95, and 2.39 Å corrected for a more accurate calculation from Ref. 6. The correction included matching of the peaks of the dipole moment functions from Refs. 6 and 7, which resulted in a shift of the above points by about 0.3 Å toward larger R.
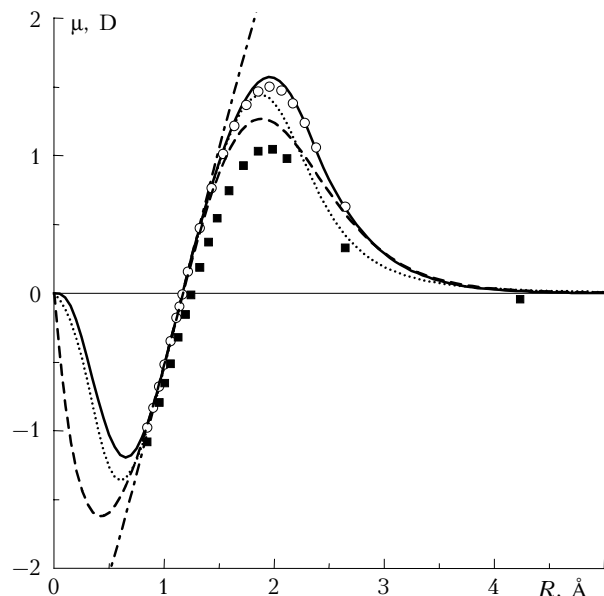
Table 1. Atomic parameters for calculation of the dipole moment functions of the CO and NO molecules, in a.u.

Parameter	C (^2P)		O (^3P)		N (^4S)
	$M_L = 0$	$M_L = \pm 1$	$M_L = 0$	$M_L = \pm 1$	$M_L = 0$
$\alpha_{zz}(L, M_L)$	9.9 [Ref. 19]	12.1 [Ref. 19]	6.1 [Ref. 19]	5.0 [Ref. 19]	7.3 [Ref. 19]
$Q_{zz}(L, M_L)$	1.42 [Ref. 19]	−0.71 [Ref. 19]	−1.02 [Ref. 19]	0.51 [Ref. 19]	0
β	0.9097 [Ref. 20]		1.0336 [Ref. 20]		1.0005 [Ref. 20]

Table 2. Parameters for calculation of the dipole moment functions of the CO and NO molecules
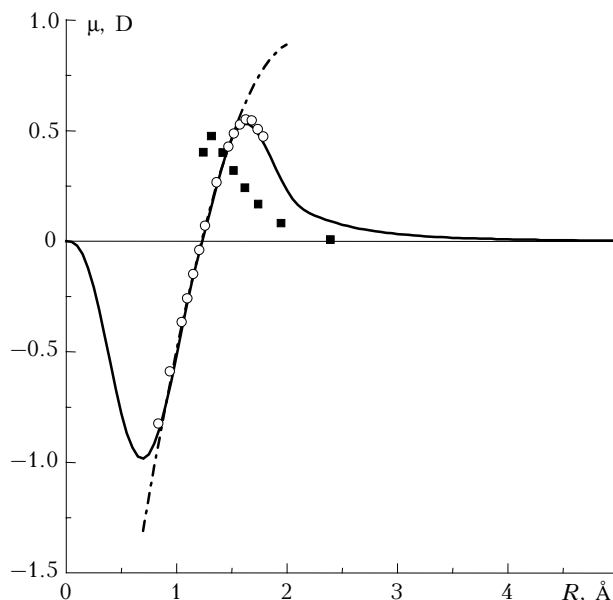
Parameter	CO ($X^1\Sigma^+$)	NO ($X^2\Pi$)
M_0, D	−0.122861 [Ref. 8]	−0.16 [Ref. 11]
M_1, D	3.614784 [Ref. 8]	2.459 [Ref. 11]
M_2, D	−0.031838 [Ref. 8]	−2.563 [Ref. 11]
M_3, D	−2.919004 [Ref. 8]	−1.029 [Ref. 11]
M_4, D	4.214029 [Ref. 8]	−
a_3, D $\cdot$ Å^{-3}	−42.484258	−24.285928
a_4, D $\cdot$ Å^{-4}	116.206827	53.470645
a_5, D $\cdot$ Å^{-5}	−122.037160	−39.607344
a_6, D $\cdot$ Å^{-6}	58.615302	9.908159
a_7, D $\cdot$ Å^{-7}	−10.829630	−
b_0, D	−32.540175	146.031407
b_1, D $\cdot$ Å^{-1}	91.324444	−446.232204
b_2, D $\cdot$ Å^{-2}	−107.446965	530.241421
b_3, D $\cdot$ Å^{-3}	65.339643	−306.580916
b_4, D $\cdot$ Å^{-4}	−19.721384	86.559755
b_5, D $\cdot$ Å^{-5}	2.314705	−9.581589
B_0, D $\cdot$ Å$^{-\delta}$	152.649127	7.265985
$\bar{C}$, D $\cdot$ Å^{-4}	0.134	2.226
R_1, Å	1.3	1.3
R_2, Å	2.4	2.2

The calculated dipole moment functions of the CO and NO molecules are depicted in Figs. 1 and 2. As can be seen from the figures, the sign of these functions alternates (direction of the dipole moment) near their equilibrium internuclear separation, what just explains small values of the dipole moments of CO and NO at the point R_e. The positive value of the dipole moment function in Figs. 1 and 2 corresponds to the polarity C^+O^- and N^+O^-. The

Fig. 1. Dipole moment function of the CO molecule: this work (solid curve), Pade approximation[13] (dotted curve), exponential form[15] (dashed curve), approximation by a power series[8] (dot-and-dash curve), *ab initio* calculation[2] (circles), *ab initio* calculation[4] (squares).

dipole moment functions calculated in this work agree well with their *ab initio* values from Ref. 2 for the CO molecule (0.85 < R < 2.65 Å) and from Ref. 6 for the NO molecule (0.83 < R < 1.79 Å). The dipole moment function of the CO molecule also agrees well with those specified in the form of the Pade approximation[13] and in the exponential form[15] in the whole range of R.

Fig. 2. Dipole moment function of the NO molecule: this work (solid curve), approximation by a power series[11] (dot-and-dash curve), *ab initio* calculation[6] (circles), *ab initio* calculation[7] (squares).

Analysis of the curves in Figs. 1 and 2 allows us to determine the limits of applicability of the dipole moment function in the form (13) with the given number of the coefficients M_i and shows that the dipole moment functions for the CO [Ref. 4] and NO [Ref. 7] molecules are likely understated.

Conclusion

The dipole moment functions of the CO and NO molecules have been calculated within the framework of the semi-empiric approach. These functions have a physically correct asymptotic behavior at small and large internuclear separations and agree with the experimental ones near the equilibrium positions of the nuclei of these molecules. The dipole moment functions obtained correctly describe alternation of the dipole moment sign. We believe that these dipole moment functions of the CO and NO molecules are now the closest to the actual ones.

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