Theoretical study of the OH radical dipole moment function at short internuclear distances

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The electric dipole moment function of the OH radical in the ground electronic state $X^2\Pi$ was *ab initio* calculated at short internuclear distances in terms of the united atom model. Calculating formulas were obtained in the first order of the perturbation theory, where matrix elements of perturbation and dipole moment operators were calculated within the *LS*- coupling approximation at wave functions of the united atom F. Energies and wave functions of the ground and excited states of the F atom for the ^1S, ^3P, and ^1D cores were calculated using the Hartree–Fock self-consistent field method (HFSCF). The obtained results were used in refinement of the semiempirical dipole moment function of the OH radical.

Introduction

The OH molecule is resulted from a series of chemical processes in the atmosphere, among which the ultraviolet-initiated photolysis of water vapor and ozone molecules can be pointed out. Since the OH molecule is a high-active radical, it plays an important role in chemistry of the atmosphere being its natural cleaner. In this connection, various physical properties of the radical should be studied. The dipole moment $\mu(R)$ as a function of internuclear distance R is one of the principal characteristics of the OH radical.

Despite the importance of the OH radical for atmospheric chemistry and ecology, there are few experimental works devoted to studying its dipole moment function.[1–4] This can be explained by difficulties in measuring spectra of this chemically-active molecule. Thus, the function of the OH radical empirical dipole moment, usually represented as the Taylor series in the neighborhood of the equilibrium position of nuclei R_e, is defined no better than up to the third derivative.[4] *Ab initio* calculations of the $\mu(R)$ function are presented much wider.[5–13] In particular, Refs. 5–8 cite the calculations of the $\mu(R)$ function in the wide range of internuclear distances R from 1.2 to 10 a.u., where the OH molecule is represented by two individual interacting atoms. Nevertheless, such calculations in the range of short internuclear distances for the OH molecule are lacking, though they are urgent for refinement of the known semiempirical $\mu(R)$ functions[14,15] describing the behavior of the OH molecule dipole moment in the entire internuclear range.

The aim of this work is the theoretical calculation of the dipole moment function of the OH radical in the ground electronic state at short internuclear distances and the refinement of the semiempirical $\mu(R)$ function[14] for the entire range of internuclear distances on the base of this calculation.

Theoretical model

The dipole moment function of the OH radical at short internuclear distances is calculated by our method,[16,17] based on the united atom model.[18,19] In this case, the dipole moment function for a molecule can be written as

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

where V_{0m} and μ_{0m} are the matrix elements of the perturbation and dipole moment operators of the molecule for wave functions of the ground Ψ_0 and excited Ψ_m states of the united atom; E_0 and E_m are the energies of these states.

Using the spherical tensor operator formalism, the perturbation and dipole moment operators in Eq. (1) can be written in the following way:

$$V = \sum_{k=0}^{\infty}\sum_{i=1}^{N} C_0^k(\theta_i,\varphi_i)\left\{\frac{Z_U}{r_i}\delta_{k0} - Z_a(-1)^k f_k(r_i,R_a) - Z_b f_k(r_i,R_b)\right\} \equiv \sum_{k=0}^{\infty} V_0^k; \tag{2}$$

$$\mu_z \equiv \mu_0^1 = \sum_{i=1}^{N} r_i C_0^1(\theta_i,\varphi_i), \tag{3}$$

where Z_a and Z_b are charges of atoms a and b; $Z_U = Z_a + Z_b$ is the charge of the united atom; $R_a = RZ_b/Z_U$, $R_b = RZ_a/Z_U$, $R = R_a + R_b$ (Fig. 1), and the function $f_k(s, t)$ is described by

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$$f_k(s,t) = \begin{cases} s^k / t^{k+1}, & s < t \\ t^k / s^{k+1}, & s \geq t. \end{cases}$$

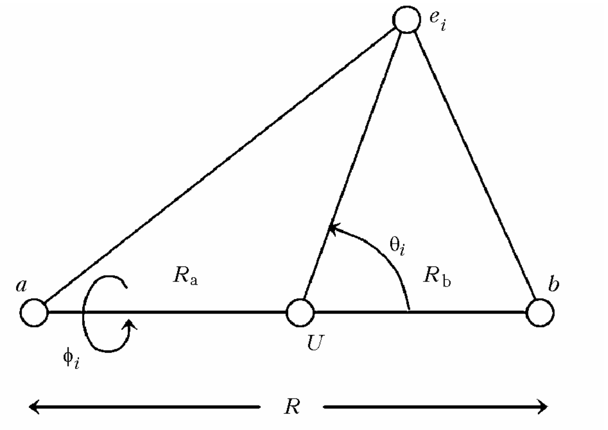

Fig. 1. Coordinate system in the united atom model. The z-axes coincides with the molecule's axes and is directed from atom a to b.

Then, in LS-coupling approximation for one-electron transitions $n_1l_1^{N_1}n_2l_2^{N_2} \rightarrow n_1l_1^{N_1-1}n_2l_2^{N_2+1}$, the matrix elements of the tensor perturbation operator take the following form[20,21]:

$$\langle \alpha LSM_SM_L | V_q^k | \alpha' L'S'M'_SM'_L \rangle =$$

$$= (-1)^{L-M_L} \begin{pmatrix} L & k & L' \\ -M_L & q & M'_L \end{pmatrix} (-1)^{S-M_S+S'-M'_S} \delta_{S'S} \delta_{M_SM'_S} \times$$

$$\times (-1)^{N_2} \sqrt{N_1(N_2+1)} G^{S_1L_1}_{S_{\text{cor}}L_{\text{cor}}} G^{S_2L_2}_{S'_2L'_2} (-1)^{l_1+L_2+L'_2+S_{\text{cor}}+S'_2+S-k} \times$$

$$\times \sqrt{(2L'_2+1)(2S'_2+1)(2L+1)(2L'+1)(2L_1+1)(2S_1+1)} \times$$

$$\times \begin{Bmatrix} S_1 & S_{\text{cor}} & \frac{1}{2} \\ S'_2 & S_2 & S \end{Bmatrix} \begin{Bmatrix} L_1 & L_{\text{cor}} & l_1 \\ L_2 & L'_2 & l_2 \\ L & L' & k \end{Bmatrix} \times$$

$$\times \left\langle R_{n_1l_1} \left\| \frac{Z_{\text{U}}}{r} \delta_{k0} - Z_{\text{a}}(-1)^k f_k(r,R_{\text{a}}) - Z_{\text{b}} f_k(r,R_{\text{b}}) \right\| R_{n_2l_2} \right\rangle \times$$

$$\times \langle l_1 \| C^k \| l_2 \rangle, \qquad (4)$$

where α, L, S, M_S, M_L are the quantum numbers of the atom ground state; n_1, l_1 and n_2, l_2 are the main and orbital quantum numbers for the electron initial and final states, respectively; N_1 and N_2 are the numbers of electrons in the n_1l_1 and n_2l_2 shells; S_{cor} and L_{cor} are the quantum numbers of a core state (the core includes filled in inner atom shells and the shell $n_1l_1^{N_1-1}$); S_1 and L_1 are the quantum numbers of the $n_1l_1^{N_1}$ shell state; S_2 and L_2 are the quantum numbers of the $n_2l_2^{N_2}$ shell state; $G^{S_1L_1}_{S_{\text{cor}}L_{\text{cor}}}$ and $G^{S_2L_2}_{S'_2L'_2}$ are the genealogical coefficients. The primed quantum numbers correspond to excited states.

Equation (4) can be also used for calculating the matrix elements of the dipole moment operator μ_0^1 by changing the integrand in a reduced matrix element in radial wave functions R_{nl} to r and setting $k = 1$ and $q = 0$.

When accounting for Eqs. (2)–(4), the dipole moment function of the OH molecule is essentially simplified:

$$\mu(R) = \sum_i \mu_i(R), \qquad (5)$$

$$\mu_i(R) = \sum_k a_{ik} \times$$

$$\times \sum_{n_2} \frac{\langle R_{2p} \| r \| R_{n_2l_2} \rangle_i \langle R_{n_2l_2} \| Z_{\text{a}} f_k(r,R_{\text{a}}) - Z_{\text{b}} f_k(r,R_{\text{b}}) \| R_{2p} \rangle_i}{(E_{2p} - E_{n_2l_2})_i}, \qquad (6)$$

where R_{2p} and E_{2p} are the radial wave function and the energy of the ground state $2p^5(^2P)$ of the united atom F; $R_{n_2l_2}$ and $E_{n_2l_2}$ are, respectively, the wave functions and energies of its excited states for each ith allowed dipole transition. Coefficients a_{ik} (k = 1, 3) for these transitions are given in Table 1. Note, that for F atom the LS-coupling approach of angular moments is properly fulfilled.

Table 1. Coefficients a_{ik} for the allowed dipole transitions of the F atom

i	$2p^5(^2P) \rightarrow 2p^4[^{2S_{\text{cor}}+1}L_{\text{cor}}]n_2l_2(^2L')$	a_{i1}	a_{i3}
1	$2p^5(^2P) \rightarrow 2p^4[^1S]n_2d(^2D)$	$\frac{2}{15}$	$-\frac{2}{35}$
2	$2p^5(^2P) \rightarrow 2p^4[^3P]n_2s(^2P)$	1	0
3	$2p^5(^2P) \rightarrow 2p^4[^3P]n_2d(^2P)$	$\frac{1}{2}$	0
4	$2p^5(^2P) \rightarrow 2p^4[^3P]n_2d(^2D)$	$\frac{9}{10}$	$\frac{9}{35}$
5	$2p^5(^2P) \rightarrow 2p^4[^1D]n_2s(^2D)$	$\frac{1}{3}$	0
6	$2p^5(^2P) \rightarrow 2p^4[^1D]n_2d(^2P)$	$\frac{1}{2}$	0
7	$2p^5(^2P) \rightarrow 2p^4[^1D]n_2d(^2D)$	$\frac{7}{30}$	$-\frac{1}{35}$

Radial wave functions R_{nl} were computed with the Hartree–Fock method using the Froese-Fischer package.[22] In this paper, the functions of the F atom ground and excited states (n_2 = 3–9) were calculated for transitions presented in Table 1. Radial integrals were calculated with the method suggested in Ref. 23.

Discussion

Based on the above-described theoretical model, the dipole moment function $\mu(R)$ of the OH radical was calculated within the internuclear distance variation range R = 0–0.4 a.u. (Fig. 2).

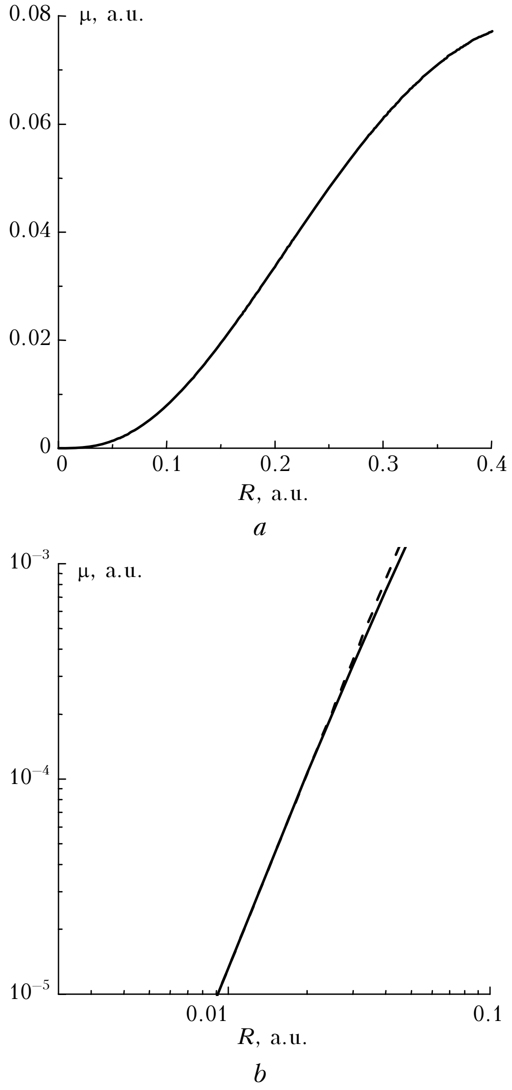

Fig. 2. Calculated dipole moment function of the OH radical at short internuclear distances: linear scale (*a*); the logarithmic scale (*b*); solid line corresponds to the *ab initio* calculation and the dashed line – to calculation by the formula $\mu(R) = AR^3$ with coefficient A = 13.2 a.u.

The positive direction of the OH radical dipole moment corresponds to the polarity H^+O^-. As is seen from Fig. 2*b*, the dipole moment function at short internuclear distances ($R \leq 0.1$ a.u.) has an asymptotical behavior $\mu(R) = AR^3$ in good agreement with the theory.[19] In this case, the calculated coefficient A equals to 13.2 a.u. We assume the function $\mu(R)$ obtained for the range $R \leq 0.15$ a.u. to be correct (see Fig. 2*a*).

The values of the $\mu(R)$ function calculated for $R \leq 0.15$ a.u. were used for refinement of the semiempirical dipole moment function[14] for the range $R \leq R_e$. In this case, the obtained function $\mu(R)$ was cubic-spline stitched with the empirical dipole moment function in the neighborhood of the equilibrium position of nuclei.[1] Calculation results for the $\mu(R)$ function within the entire range R are shown in Fig. 3 and Table 2.

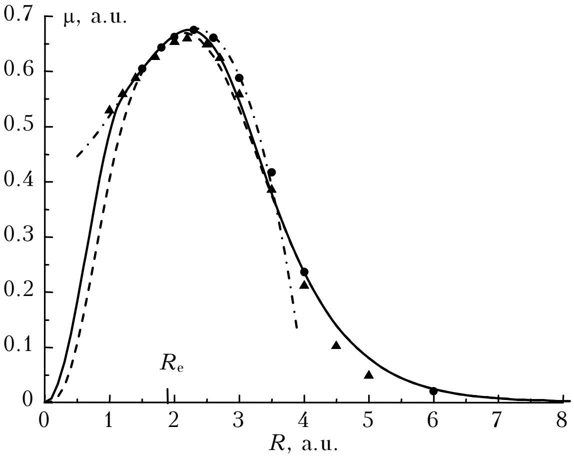

Fig. 3. Dipole moment function of the OH radical: this work (solid line); Ref. 14 (dashed line); calculated using the Taylor series with the coefficients defined in Ref. 1 (dashed-dotted line); *ab initio* calculated[7] (triangles); *ab initio* calculated[5] (circles).

Table 2. Dipole moment function of the OH radical (a.u.)

R	$\mu(R)$	R	$\mu(R)$
0.0	0.0000	2.8	0.6022
0.2	0.0338	3.0	0.5461
0.4	0.1244	3.2	0.4811
0.6	0.2481	3.4	0.4129
0.8	0.3786	3.6	0.3470
1.0	0.4895	3.8	0.2875
1.2	0.5544	4.0	0.2362
1.4	0.5879	4.5	0.1401
1.6	0.6190	5.0	0.0802
1.8	0.6455	5.5	0.0448
2.0	0.6653	6.0	0.0248
2.2	0.6751	7.0	0.0078
2.4	0.6689	8.0	0.0028
2.6	0.6443	9.0	0.0013

The analysis of Fig. 3 shows that the obtained function describes the dipole moment at short internuclear distances more correct than the semiempirical function.[14]

Conclusion

Basing on the *ab initio* calculations of the dipole moment function of the OH radical at short internuclear distances, the behavior of the function $\mu(R)$ was ascertained at $R \to 0$, which allowed us to obtain more physically valid semiempirical dipole moment function within the internuclear distances range $R \leq R_e$. As a result, the complete dipole moment function, defined for the entire variation range of the OH radical internuclear distances will be more correct. Such complete function can be used for calculating the Einstein coefficients and probabilities of rovibrational transitions within a wide variation range of rotational quantum numbers. The dipole moment of the OH radical, being in excited rotational states, can also be calculated using the obtained function $\mu(R)$.

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