

Rydberg states of OH radical

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We study Rydberg states of radical in adiabatic (rotational Born–Oppenheimer) approximation as well as in the inverse limit. The needed value, $d = 0.833$, of the OH⁺ cation's dipole moment was calculated using the RCCSD(T)/aug-cc-pV5Z. Our calculations show that a dipole moment of this magnitude influence weakly on the energies of the Rydberg states. The exception are the states originating from s-states in the central-symmetric field, which are influenced significantly by the cation dipole moment. In the inverse Born–Oppenheimer limit, we study in detail the dependence of the Rydberg spectrum upon the total angular momentum, J , of the molecule. This dependence substantially differs from the well-known dependence, $\sim J(J + 1)$, of the rotator energy on its total momentum.

Keywords: polar molecules, multipole moments, polarizability, hydroxyl.

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Introduction

Processes involving highly excited (Rydberg) states of atoms and molecules are important in many branches of physics and chemistry. This also applies to the OH radical, which is present in appreciable amounts in the atmosphere of the Earth and other planets. The hydroxyl radical is formed in the atmosphere as a result of photolysis [1] or dissociative excitation of water molecules by free electrons [2]. Note that an additional mechanism for the formation of the hydroxyl radical is possible in a gas-discharge plasma due to the energy transfer from metastable argon atoms to water molecules [3]. The OH radical promotes the formation of nitrogen oxides from atmospheric nitrogen [4]. OH clouds occupy significant volumes in the Universe, so the observation of Rydberg OH spectra can provide useful information about the physical conditions in these objects. Daily fluctuations in the OH absorption in the lunar atmosphere in the near-IR range can provide important information about the formation of water molecules as a result of the absorption of solar wind protons [5], the fall of meteorites or comets with an icy nucleus [5], or as a result of photolysis [7–9]. Besides, this radical is considered as one of the candidates for determining the change in world constants over time (see, for example, [10–15]).

One of the main problems associated with finding the Rydberg spectra of polar molecules is due to the mixing by the dipole moment of the molecular core of the states of the Rydberg electron (RE) with different orbital momenta. Several solutions of this problem are known, for example, the multichannel quantum defect theory (MQDT) proposed by Seaton [16,17]. This theory has been developed by many

authors, primarily for non-polar molecules [18–22]. Later, MQDT was applied to some polar molecules, in particular, NO [23], CaF [24–29], BaF [15,30–33], CaCl [34–36], SO [37] etc.

MQDT is applicable in the region of large quantum numbers of RE, $n \gg 1$, and has a relatively high accuracy in this region. However, in some cases, computationally simpler approaches can be applied. One of these approaches is based on an approximate representation of the potential of the molecular core as a superposition of the potentials of a point charge and a point dipole. Under this approach analytical solutions of the Schrödinger equation for RE were obtained in two limiting cases.

One of these limiting cases is the adiabatic approximation, also known as the Born–Oppenheimer approximation (BOA), when the core rotation is much slower than the motion of RE. The corresponding analytical solution was given in the papers [38,39]. Just in the papers [38,39] RE states with integer orbital momenta were used to construct states with some effective non-integer, in the general case, orbital momenta which take into account the effect of states mixing by the dipole moment of the core.

The second limiting case is the inverse Born–Oppenheimer approximation (IBOA), when the core is considered to be quickly rotating compared to the RE motion. Such an extreme case is possible if the principal quantum number of RE is large enough. The analytical solution to the Schrödinger equation for IBOA was obtained in [40]. When going from BOA to IBOA, a radical rearrangement of the RE spectrum occurs, in particular, its dependence on the dipole moment of the core. We emphasize that IBOA in our case is associated with the slow motion corresponding to electronic degrees

of freedom compared to rotational, but not vibrational one, as it is usually understood for low-excited states of molecules [41–43].

Calculations of the Rydberg spectra of the SO molecule in the limit cases of BOA and IBOA are presented in [44]. In this work, similar calculations are carried out for OH radical.

As the principal quantum number of RE increases, the level shifts generated by the quantum defect decrease in absolute value. When they become comparable with the splitting of core Λ -doublet, anomalies can be observed in the Rydberg spectrum of the polar molecule, which were discussed in the general case in [45], and for SO molecule in the paper [44]. In the present paper these anomalies are not considered. Note only that it is the transition between Λ -double levels in the OH radical (wavelength $\simeq 18$ cm) that was analyzed in the papers [10–15].

Also, this paper does not consider the potential energy curves for the OH molecule and its vibrational spectra. Correspondingly, spectrum perturbations associated with predissociation are not analyzed. The predissociation of the $A^2\Sigma^+$ -states of the OH radical was studied theoretically and experimentally in a number of papers (see, for example, [46] and references therein), however, the predissociation of higher Rydberg states, which are the subject of this paper, requires special consideration.

In this paper, except of specified cases, the atomic system of units is used.

Main equations

Adiabatic limit (BRA)

To take into account the mixing of RE states with different orbital momenta l and dipole moment d , in papers [38,39,47] instead of the usual spherical functions $Y_{lm}(\theta, \varphi)$ the angular functions are introduced

$$Z_{\text{BOA}}(d; \theta, \varphi) = \sum_{l=|m|}^{\infty} a_l Y_{lm}(\theta, \varphi), \quad (1)$$

where m is the projection of the orbital momentum of RE onto the direction z of the dipole moment of the molecular core, and the coefficients a_l are the eigen vectors of the linear tridiagonal system of homogeneous algebraic equations corresponding to the eigen values \mathcal{L} :

$$l(l+1)a_l + 2d \sum_{l'=l\pm 1} \left(\frac{2l'+1}{2l+1} \right)^{1/2} \times C_{l'010}^{l0} C_{l'm10}^{lm} a_{l'} = \mathcal{L} a_l, \quad |m| \leq l < \infty. \quad (2)$$

The eigen values \mathcal{L} and the eigen vectors of the system of equations (2) will be numbered by integers L varying within the same limits as the summation index l in (2),

namely $|m| \leq L < \infty$. Moreover, we choose the numbering so that for $d \rightarrow 0$

$$\mathcal{L}^{(L)} \rightarrow L(L+1), \quad a_l^{(L)} \rightarrow \delta_{ll}. \quad (3)$$

Generally, it is convenient to introduce the effective orbital momenta \tilde{L} defined by the relation

$$\mathcal{L}^{(L)} = \tilde{L}(\tilde{L}+1), \quad \tilde{L} = \sqrt{\mathcal{L}^{(L)} + 1/4} - 1/2. \quad (4)$$

The RE spectrum is expressed in terms of \tilde{L} by the formula

$$\varepsilon_{vL} = -1/2v^2, \quad v = n_r + \tilde{L} + 1. \quad (5)$$

Here, $n_r = 0, 1, \dots$ is the radial quantum number. Note that for $\mathcal{L}^{(L)} < -1/4$, which is possible for rather large dipole moment, the RE spectrum, and with it the spectrum of the entire molecule, becomes complex. This means, as known, the instability of the system, namely, the RE fall to the center of the molecular coordinate system [48]. As applied to the problem considered here, the occurrence of such behavior indicates the inapplicability of the point core approximation for states with $\mathcal{L}^{(L)} < -1/4$. This problem is considered in more detail, for example, in the paper [49].

The contribution of the quadrupole moment and core polarizability to the quantum defect in the first approximation of perturbation theory:

$$\mu_Q = \frac{2(L(L+1) - 3m^2)}{L(L+1)(2L-1)(2L+1)(2L+3)} Q_{zz}, \quad (6)$$

$$\mu_{\text{pol}} = \frac{12(1 - L(L+1)/3n^2)}{L(L+1)(2L-1)(2L+1)(2L+3)} \times \left(\frac{\bar{\alpha}}{2} + \frac{\gamma}{3} \frac{L(L+1) - 3m^2}{(2L+1)(2L+3)} \right), \quad (7)$$

$$\bar{\alpha} = \frac{2\alpha_{\perp} + \alpha_{\parallel}}{3}, \quad \gamma = \alpha_{\parallel} - \alpha_{\perp}, \quad n = n_r + L + 1.$$

The above expressions for μ_Q and μ_{pol} are valid for $L \neq 0$. For $L = 0$, we have $\mu_Q = 0$, and the corresponding expression for μ_{pol} turns out to be divergent, which also indicates that the point core approximation is inapplicable in this case.

Inverse rotational Born–Oppenheimer approximation (IBOA)

The solution to the Schrödinger equation for the electron moving in a Coulomb field and in the field of a rapidly rotating point dipole was found in paper [40] for a symmetric top. For the diatomic molecule considered in this paper the general formulas are somewhat simplified.

According to paper [40] the wave function of molecule in IBOA is sought in the form:

$$\Psi_{JM}^{j\lambda} = \sqrt{\frac{2j+1}{8\pi^2}} R(r) \sum_{l_j z m} C_{j j z l m}^{JM} D_{\omega_j z}^j(\Omega) Y_{lm}(\mathbf{r}/r) a_l^x. \quad (8)$$

Here, the index κ denotes the set of indices (J, j, ω), J is the total moment of the molecule, M is its projection onto the z axis of the laboratory coordinate system (LCS), j, j_z is total moment of the core and its projection onto the z axis of LCS respectively, ω is projection of core moment on molecule axis coinciding with direction of dipole moment, D is matrix of finite rotations depending on the Euler angles of the core Ω , $R(r)$ is radial wave function of RE. Unlike [38,39], the solution to the Schrödinger equation obtained in [40] was reduced to finding the eigen values \mathcal{L}_κ and the eigen vectors $\{a_i^\kappa\}$ of finite system of linear algebraic equations defining the angular function $Z_{IBOA}(d; \theta, \varphi)$, similar to (2):

$$l(l+1)a_i^\kappa + 2(-1)^{2j}d\omega \left[\frac{(2j+1)(2l+1)}{j(j+1)} \right]^{1/2} \\ \times \sum_{l'=l\pm 1} C_{l0l0}^{l'0} W(j1Jl'; j1) a_{l'}^\kappa = \mathcal{L}_\kappa a_i^\kappa, \\ |J-j| \leq l \leq J+j, \quad (9)$$

where W are Racah coefficients. The dependence of the eigen values \mathcal{L}_κ on J , which follows from this formula, determines the dependence of the molecule energy on its total moment. Since we do not consider the RE spin, it follows from the properties of the Clebsch–Gordan coefficient in formula (8) that the total momentum J of molecule is integer or half-integer, depending on whether the core moment j is integer or half-integer.

The eigen values and eigen vectors of the system of equations (9) will also be enumerated by integers L , which now vary within $|J-j| \leq L \leq J+j$. By analogy with formulas (3), (5)

$$\mathcal{L}_\kappa^{(L)} \rightarrow L(L+1), \quad a_i^{\kappa(L)} \rightarrow \delta_{Ll}, \quad \text{at } d \rightarrow 0, \\ \varepsilon_{\kappa vL} = -1/2v^2, \quad v = n_r + \mathcal{L} + 1, \quad n_r = 0, 1, \dots \quad (10)$$

Note that for $\omega = 0$, which is possible for integer j , equations (9) give $\mathcal{L}_\kappa = l(l+1)$, which differs from limiting values (10) by designations only. In other words, at $\omega = 0$ the dipole moment does not affect the RE motion. The physical meaning of this fact is quite clear: at $\omega = 0$ the dipole moment of the core is perpendicular to the axis of its rotation, and the value of the dipole moment is averaged when the core rotates rapidly.

The total energy of the molecule is given by

$$E_{\kappa vL} = B j(j+1) + \varepsilon_{\kappa vL}, \quad (11)$$

where B is rotational constant of the core. Since $\varepsilon_{\kappa vL} < 0$, it follows from formula (11) that below each rotational level of the core, with moment j , there is a Coulomb-like spectrum of RE split in L and J . Equations (2), (9) are the main formulas in the present work. After their solution, the Rydberg spectra are found by formulas (5), (10). More complex cases of the relationship between intramolecular angular momentums are considered in [50].

Dipole and quadrupole moments and polarizability of radical-cation OH⁺

To solve equations (2), (9), it is necessary to know the dipole moment of the OH⁺ radical, as well as its quadrupole moment and polarizability (to estimate quantum defects using formulas (6) and (7)). We used two groups of methods to calculate the multipole moments.

In the first case, the calculation was carried out using modern packages for quantum-chemical calculations: Gaussian [51], MOLPRO [52] and NWChem [53]. Such methods as density functional theory (DFT), Møller–Plesset Perturbation Theory (MP2), coupled cluster method (CCSD), configuration interaction (QCISD) were used. We used such an equilibrium internuclear distance R_e , which was obtained by optimization under the method used.

In the second case, for calculation we used the one-configuration finite-difference Hartree–Fock method x2DHF [54], which gives the Slater asymptotic form of the radial wave functions. A reference value [55] was taken for R_e .

The calculations were carried out in the system of the nuclear center of charge. For a different choice of the coordinates origin, which is important for calculating the dipole moments of systems with excess charge, see [56–58]. z axis was chosen to be directed from O to H. Then, for a given electron density $\rho_e(\mathbf{r})$, for the dipole and quadrupole moments, we have, respectively

$$d = - \int z \rho_e(\mathbf{r}) d^3r, \\ Q_{zz} = \frac{8}{9} R_e^2 - \frac{1}{2} \int \rho_e(\mathbf{r}) (3z^2 - r^2) d^3r. \quad (12)$$

The first term in Q_{zz} is due to the contribution of positive nuclear charges. The second term is determined by the electronic configuration. We consider the ground electronic term $X^3\Sigma^-$ with configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi_{+1} 1\pi_{-1}$, where π -electrons are unpaired and form a spin triplet.

The static polarizability is calculated here by numerical differentiating of the induced dipole moment with respect to the external field strength.

The calculation results are given in Table 1. For quantum chemical calculations, such methods/basis sets were used that for the dipole moment of the neutral radical OH ensure difference from the experimental value $d(\text{OH}) = 0.6531$ a.u., recommended by NIST [59], less than 1%. For the moments d and Q_{zz} in the OH⁺ ion, lines 1–6 show the results of calculations with methods/basis sets that give the equilibrium internuclear distance R_e , which differs from the tabular $R_e = 1.029$ Å within 0.1%. The results in lines 1–5 were obtained using the MOLPRO package, and in line 6 with the MP2 method — using the Gaussian package. Methods 3–6 belong to the class of post-Hartree–Fock. The methods of coupled clusters CCSD and the configurations interaction QCISD are non-perturbative multi-configuration methods.

Table 1. Equilibrium internuclear distance, permanent dipole d and quadrupole Q_{zz} moments, and polarizabilities of OH^+ radical cation in the system of nuclear center of charge. z axis is directed from O to H; NIST values are taken from the database [59], other values are calculated in this paper („t.p.“)

№	Method / basis set	R_e , Å	d , a.u.		Q_{zz} , a.u.		Polarizability, a.u.		
			t.p.	NIST	t.p.	NIST	α_{\perp}	α_{\parallel}	$\bar{\alpha}$
1	wB97X-D/ d-aug-cc-pVQZ	1.0289	0.7904		1.3405		3.4563	4.9698	3.9608
2	B97D3/ Def2TZVPP	1.0292	0.7954	0.784	1.3351	1.342	2.9949	4.9224	3.68 [59]
3	QCISD/ 6-31G(2df,p)	1.0294	0.8410	0.841	1.3660		3.0566	4.7472	3.6201
4	CCSD/ aug-cc-pVTZ	1.0290	0.8338	0.792	1.3507	1.334	3.4265	5.0139	3.9556
5	CCSD/ d-aug-cc-pVTZ	1.0291	0.8331	0.792	1.3526	1.335	3.4191	5.0041	3.9474
6	MP2/ d-aug-cc-pVDZ	1.0276	0.8299		1.3435	1.326	3.4530	4.9146	3.94 [59]
7	RCCSD/ aug-cc-pVTZ	1.0289	0.8343		1.3837		3.4558	5.0352	3.9823
8	RCCSD/ d-aug-cc-pVTZ	1.0290	0.8336		1.3853		3.4470	5.0254	3.9731
9	CCSD+T(CCSD)/ aug-cc-pVTZ	1.0277	0.7912			1.319	3.4414	4.9984	3.9604
10	CCSD+T(CCSD)/ d-aug-cc-pVTZ	1.0285	0.7915			1.322	3.4400	4.9862	3.9554
11	MCSCF [60]	1.031	0.913						
12	x2DHF	1.029 [54]	0.8394		1.4336				

We also studied additionally RCCSD methods that prevent „spin contamination“ in systems with open shells. As lines 7, 8 show, this leads to a change in the dipole moment by less than 0.1% and in the quadrupole moment — by $\sim 1\%$.

DFT methods reduce the calculation time by 2–3 orders and give for R_e results comparable in accuracy ($< 0.1\%$) with RCCSD(T) results.

Perturbative account for triple excitations of electrons by CCSD(T) and QCISD(T) methods led to a change in the equilibrium internuclear distance by several percent. The reason for this discrepancy may be the specifics of these methods use (see below).

Another multi-configuration method for accounting for triple excitations CCSD+T(CCSD), performed using the aug-cc-pVTZ basis set in the NWChem package, which proved to be efficient, also gave acceptable values for internuclear distances R_e in OH and OH^+ , and for the dipole moment OH. However, the dipole moment of the radical cation OH^+ (lines 9, 10 in Table 1) turns out

to be smaller and comparable to that obtained by density functional methods.

We also tested the capabilities of the many-body perturbation theory of 4th order MBPT4 implemented in NWChem package. Despite the good reproduction of the internuclear distance, the dipole moment of the neutral radical OH turned out to differ from the tabulated value by $\sim 10\%$ when using correlation-consistent basis sets. Therefore, we did not use the MBPT4 method to calculate the multipole moments of the radical cation OH^+ .

For comparison, the values of R_e and d are also given, they were obtained in the paper [61] by the multi-configuration self-consistent field method MCSCF within the Ruitaan–Hartree–Fock approach [60] (line 11 in Table 1). In the cited paper 7 configurations were involved, which in Cartesian coordinates look like: $3\sigma^2 1\pi_x 1\pi_y$, $4\sigma^2 1\pi_x 1\pi_y$, $3\sigma^2 \{1\pi_x 2\pi_y - 1\pi_y 2\pi_x\}$, $3\sigma^2 2\pi_x 2\pi_y$, $^1(3\sigma 4\sigma) \{1\pi_x 2\pi_y - 1\pi_y 2\pi_x\}$, $^1(3\sigma 4\sigma) 1\pi_x 1\pi_y$, $^3(3\sigma 4\sigma)^3(1\pi_x 1\pi_y)$.

Line 12 in Table 1 shows the data obtained by the finite-difference Hartree–Fock method in spheroidal coordinates proposed in the paper [54].

Unfortunately, the dipole and quadrupole moments found by various post-Hartree–Fock methods: coupled clusters CCSD, configurations interactions QCISD, and Müller–Plesset MP2 (lines 3–6 in Table 1), with the basis sets used in [59] for OH, have a rather large spread of values ($d = 0.834 \pm 0.004$, $Q_{zz} = 1.364 \pm 0.016$).

Nevertheless, the coupled clusters method mentioned above is recognized as one of the most accurate approaches in modern quantum chemistry. The accuracy of calculation of most molecular parameters, in particular, polarizabilities, is comparable with the accuracy of experimental methods [62]. However, the correlation energy cannot be correctly taken into account even by the CCSD(T) method in small and medium size basis sets. For this reason, using CCSD(T)/aug-cc-pVTZ worsened the result for the equilibrium internuclear distance compared to CCSD/aug-cc-pVTZ.

Table 2 lists the equilibrium internuclear distances, multipole moments, and static polarizability of the radical cation OH⁺ calculated by the wB97X–D density functional theory and by RCCSD(T) method with different basis sets x-aug-cc-pVXZ.

The RCCSD method demonstrates good convergence R_e , d , and Q_{zz} of the radical cation OH⁺ with increasing quality parameter X in the basis set x-aug-cc-pVXZ. There is no significant difference between *-pV5Z and *-pV6Z. For the radical cation OH⁺ the polarizability is practically insensitive to the number of diffuse functions x per orbital. There are no differences already between x = 1 (aug-*) or 2 (d-aug-*).

For multipole moments the convergence of both methods also takes place. However, DFT gives underestimated values compared to RCCSD(T) by 5% for dipole moments and by 3% for quadrupole moments.

For static polarizabilities the results of both methods are comparable. However, in contrast to RCCSD(T) the convergence of DFT results with increasing X turns out to be slower and nonmonotonic.

The equilibrium internuclear distance $R_e = 1.0280$ Å differs from the that proposed by NIST [59] by less than 0.1%. The importance of the exact reproduction of the parameter R_e is shown in Table 2 for calculating the multipole moments as functions of the internuclear distance by the method RCCSD(T)/aug-cc-pV5Z. It is easy to see that change in the internuclear distance in the vicinity of the equilibrium value by 10% leads to change in the dipole moment by the same order of magnitude, and in the quadrupole moment by ~ 34%. Such sensitivity of moments to the choice of internuclear distance was noted in [63].

Thus, to calculate the OH⁺ parameters where not otherwise stated, it is sufficient to limit by RCCSD(T)/aug-cc-pV5Z. The values of the multipole moments, $d = 0.833$, $Q_{zz} = 1.382$, will be used further

Table 2. Equilibrium internuclear distance (in Å), permanent dipole d and quadrupole Q_{zz} moments of the radical-cation OH⁺ in the system of nuclear center of charge and static polarizability (all in atomic units); z axis is directed from O to H; basis sets x-aug-cc-pVXZ

x	X	R_e	d	Q_{zz}	α_{\perp}	α_{\parallel}	$\bar{\alpha} = \frac{1}{3} \text{Sp}\alpha$
wB97X–D							
1	T	1.0299	0.7907	1.3381	3.4606	5.0069	3.9760
	Q	1.0289	0.7904	1.3405	3.4563	4.9698	3.9608
	5	1.0286	0.7904	1.3391	3.4668	4.9735	3.9690
	6	1.0286	0.7900	1.3392	3.4621	4.9685	3.9642
2	T	1.0300	0.7900	1.3415	3.4554	4.9911	3.9673
	Q	1.0289	0.7904	1.3392	3.4551	4.9686	3.9596
	5	1.0286	0.7903	1.3392	3.4669	4.9734	3.9691
	6	1.0286	0.7900	1.3392	3.4622	4.9690	3.9645
RCCSD(T)							
1	T	1.0312	0.8366	1.3933	3.4558	5.0352	3.9823
	Q	1.0283	0.8329	1.3839	3.4328	4.9742	3.9466
	5	1.0280	0.8328	1.3824	3.4250	4.9572	3.9357
	6	1.0280	0.8327	1.3824	3.4241	4.9537	3.9340
2	T	1.0313	0.8359	1.3949	3.4470	5.0254	3.9731
	Q	1.0283	0.8329	1.3839	3.4285	4.9721	3.9430
	5	1.0280	0.8328	1.3826	3.4247	4.9572	3.9355
	6	1.0280	0.8328	1.3824	3.4236	4.9539	3.9337

Table 3. The functions of the dipole d and quadrupole Q_{zz} moments of the radical-cation OH⁺ in the nuclear center of charge system found within the CCSD(T)/aug-cc-pV5Z; axis z is directed from O to H

R , Å	d , a.u.	Q_{zz} , a.u.
0.9252	0.7326	0.9804
0.9509	0.7552	1.0736
0.9766	0.7787	1.1712
1.0023	0.8031	1.2729
1.0280	0.8328	1.3824
1.0537	0.8548	1.4892
1.0794	0.8820	1.6040
1.1051	0.9102	1.7231
1.1308	0.9394	1.8468

to calculate the parameters of the Rydberg states of OH radical.

Rydberg spectra

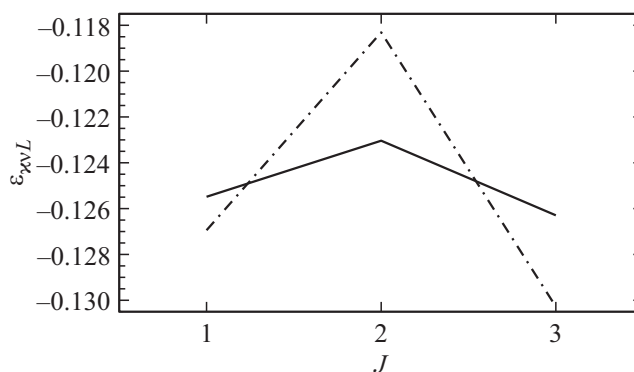
Region of BOA

In this and the next Sections we consider the contribution of the dipole moment of the molecular core to the Rydberg spectra of OH radical. RE states are usually divided into penetrating and non-penetrating. For the former one the short-range interaction of RE with the cation core is essential, while for the latter one this interaction is small. It is known from the literature (see, for example, [25,64]) that for diatomic molecules, RE states with orbital momenta $l \geq 3$ can be considered as non-penetrating. In the BOA limit this means that the use of equations (2) for calculating the RE spectra at $|m| \geq 3$ is quite justified. Note that the description of penetrating states was carried out in some papers within the framework of rather simple models (for atoms, for example, see [65]).

Table 4 lists the values of the parameters of the Rydberg states of OH radical in the BOA limit. Projections from the interval $0 \leq |m| \leq 2$ correspond to penetrating states. For a possible comparison of RE parameters with these values of $|m|$ with experiment, it is necessary to take into account the short-range interaction of RE with the core. As can be seen, for a state with $m = 0$ the effective orbital momentum \tilde{L} corresponding to $L = 0$ is complex. As mentioned above, this is due to violation of the point dipole approximation. For non-penetrating states, we present the results for only one value $|m| = 3$, since it is clear that already in this case the difference between the effective orbital momentum \tilde{L} and the principal quantum number ν from integer values is small. The same conclusion is applied to the contribution of the quadrupole moment to the principal quantum number ν . For the SO molecule this contribution was considered in paper [44], and turned out to be small in the above sense.

Region of IBOA

Let's now analyze the IBOA region. Table 5 lists the parameters of the Rydberg states similar to those given in Table 4. Since the ground state of the OH⁺ cation is a triplet, the projection of the total angular momentum onto the axis of the molecule is $\omega \geq 1$. As can be seen, the dipole moment of the core affects the states $L = 0$ most significantly, which is quite natural. In the case of $\omega = j = J = 2$ for this state, even a „drop to the center“ occurs, which relates to the complexity of the effective orbital momentum \tilde{L} and the inapplicability of the point dipole approximation. Note the negativity of \tilde{L} for $L = 0$ for other values of the parameters ω, j, J . This is due to the fact that at $L = 0$ there is practically no centrifugal repulsion of RE from the core, and the dipole moment attracts RE to the core.



RE energy $\varepsilon_{\nu L}$ vs. total momentum of molecule J . Solid line: $\omega = 1$, dashed line: $\omega = 2$. In both cases $j = 2, L = 1$.

Molecule energy vs. total angular momentum

The Figure shows the RE energies, determined by the formula (10), vs. total momentum of the molecule J for the values $\omega = 1, 2; j = 2, L = 1$. Numerical data are taken from Table 5. As can be seen, these dependencies fundamentally differ from $\sim J(J + 1)$ dependencies typical for rotator energies. Unfortunately, obtaining the values of rotational energies for larger values J is not possible due to the small difference of RE spectrum from the pure Coulomb spectrum.

Conclusion

The calculations performed show that for molecules with dipole moment of the same order as that of the OH radical, $d \approx 0.8$ a.u., the mixing of the states of Rydberg electron with different orbital momenta is relatively small. An exception in the range of applicability of the Born–Oppenheimer approach is the states with $m = L = 0$, for which, however, the point dipole approximation is inapplicable. A similar

Table 4. Parameters of Rydberg states of OH radical in the BOA limit, the quantum-chemical calculation of the static polarizability of OH⁺ was performed by method RCCSD(T)/aug-cc-pV6Z

$ m $	L	\tilde{L}	$\mu_d = L - \tilde{L}$	μ_Q	μ_{pol}
0	0	$-0.5 + 0.392941i$	–	–	–
	1	1.071	-0.071	0.184	0.678
	2	2.014	-0.014	0.026	0.030
1	1	0.954	0.046	-0.092	-0.064
	2	2.006	-0.006	0.013	0.030
	3	3.003	-0.003	0.007	0.005
2	2	1.987	0.013	-0.026	-0.028
	3	3.000	0.000	0.000	0.005
	4	4.001	-0.001	0.002	0.001
3	3	2.994	0.006	-0.011	-0.004
	4	3.999	0.001	-0.001	-0.001
	5	5.000	0.000	0.000	0.000

Table 5. Parameters of Rydberg states of the OH radical in IBOA limit

ω	j	J	L	\tilde{L}
1	1	1	0	−0.307
			1	1.051
			2	2.012
1	1	2	1	0.966
			2	2.011
			3	3.007
1	1	3	2	1.987
			3	3.004
			4	4.004
1	2	1	1	0.996
			2	2.001
			3	3.001
1	2	2	0	−0.082
			1	1.016
			2	2.003
			3	3.001
			4	4.001
1	2	3	1	0.990
			2	2.002
			3	3.001
			4	4.001
			5	5.000
2	2	1	1	0.984
			2	2.005
			3	3.003
2	2	2	0	−0.5 + 0.171i
			1	1.056
			2	2.011
			3	3.004
			4	4.002
2	2	3	1	0.959
			2	2.008
			3	3.005
			4	4.003
			5	5.002

conclusion follows for the states $\omega = j = J = 2$, $L = 0$ in the region of the inverse Born–Oppenheimer approximation. The performed calculations of rotational energies of OH Rydberg states show their fundamental difference from the spectra of the quantum rotator $\sim J(J + 1)$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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