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Numerical multiconfiguration self-consistent field study of the total (electronic and nuclear) parallel polarizability and hyperpolarizability for the OH, OH⁺, OH⁻

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Vibrational contributions to the molecular polarizability and hyperpolarizabilities are calculated for OH, OH⁺, and OH⁻ for an electric field directed along the bond axis. It was found that vibrational averaging of the polarizability works reasonably well for OH and OH⁻, but fails for OH⁺, giving a result 16% to low. For the hyperpolarizabilities, the vibrational averaging strongly underestimates the vibronic contribution, whose size can exceed the electronic contribution, and therefore disqualifies this procedure for evaluation of these types of higher-order molecular properties.

I. INTRODUCTION

There is significant interest on the experimental side in the theoretically predicted polarizabilities and hyperpolarizabilities. This stems from intensifying studies in recent years on nonlinear optical phenomena. For example, the third-order nonlinear susceptibility $\chi^{(3)}$, which mediates a wide range of nonlinear-optical processes, is the macroscopic expression of the microscopic second hyperpolarizability tensor γ, which can be obtained from a quantum-mechanical calculation. Recently, there has been much theoretical activity directed towards gaining an understanding of the various components of γ for small molecules by means of *ab initio* calculations.[1–13] It was established[4] that, while vibronic contribution to the molecular polarizability α is likely to be very small, the appropriate contributions to the first hyperpolarizability β, and especially to the second hyperpolarizability γ, are significant, and can be several times larger than the electronic part. Such a large nuclear contribution to the first nuclear hyperpolarizability is a physically significant phenomenon for static electric fields.

It should be noticed that there is more than one type of vibrational correction. To illustrate this, Pandey and Santry[1] derived formulas for vibronic contributions for molecular polarizabilities and hyperpolarizabilities using the harmonic oscillator approach and the second-order perturbation theory. The dominant terms in their expansions for the parallel vibrational polarizability and first and second hyperpolarizability for a diatomic system are

$$\alpha_v = \frac{1}{4a^2}\left(\frac{\partial^2\alpha}{\partial R^2}\right)_0 + \frac{1}{a^2\hbar\omega}\left(\frac{\partial\mu}{\partial R}\right)_0^2, \qquad (1)$$

$$\beta_v = \frac{1}{4a^2}\left(\frac{\partial^2\beta}{\partial R^2}\right)_0 + \frac{3}{a^2\hbar\omega}\left(\frac{\partial\mu}{\partial R}\right)_0\left(\frac{\partial\alpha}{\partial R}\right)_0, \qquad (2)$$

$$\gamma_v = \frac{1}{4a^2}\left(\frac{\partial^2\alpha}{\partial R^2}\right)_0 + \frac{12}{a^2\hbar\omega}\left(\frac{\partial\alpha}{\partial R}\right)_0^2, \qquad (3)$$

where $a = (m\omega/\hbar)^{1/2}$, m is the reduced mass, ω the frequency of the vibration, μ the dipole moment, α the electronic polarizability, β the first hyperpolarizability, and γ the second hyperpolarizability. The leading terms in Eqs. (1)–(3) originate from the vibrational averaging theory as discussed by Kern and Matcha.[14] One can easily realize that by ex-

panding the appropriate electronic quantity in the Taylor series with respect to the internuclear separation around the equilibrium distance and then averaging it over the ground vibronic state. The zero-order term in this expansion is the value of the appropriate polarizability calculated at the equilibrium. The first-order term vanishes because the first derivative of the electronic energy is zero at the equilibrium separation. The second-order term is, therefore, the first nonstandard vibrational contribution to the polarizability considered, and gives rise to the second terms in Eqs. (1)–(3). These terms depend upon the first derivatives of the dipole moment, the polarizability, and the hyperpolarizability with respect to the bond distance calculated at the equilibrium. They represent the lowest order contributions of the interaction between the applied external field and the vibrational structure of the molecule, which leads to small changes in the molecule's geometric structure and shifts its vibrational levels.

We name the sum of the electronic and nuclear polarizabilities the total molecular polarizability. There are three ways to calculate this quantity[8]: The first two are based on the Born–Oppenheimer approximation, with the third being a nonadiabatic approach. The first is the traditional averaging of the electronic property over the vibrational motion and incorporating the interaction of the nuclear motion with the field via perturbation theory.[15] Most of the previously reported polarizability calculations have been done with this approach. In the second method, recently proposed by us,[4] one generates the field-dependent electronic energy for various nuclear separations and then solves the nuclear Schrödinger equation for the field dependent vibrational levels, which are subsequently used to calculate the total molecular polarizability by numerical differentiation with respect to the electric field strength. The third nonadiabatic method[9] is identical to the second one, except it does not separate the electronic and the nuclear motion, and, therefore, although potentially exact, is at present limited to three-body systems (e.g., H_2^+).

This paper presents our further studies on total molecular polarizabilities and hyperpolarizabilities. Following our rather surprising discovery that the second parallel hyperpolarizability of the H_2^+ cation is comprised almost exclusively

of the vibrational component[4,9] (the electronic contribution being only -41 a.u. and the nuclear contribution being 2.3×10^3 a.u.), we shall now present a study on the total polarizabilities and hyperpolarizabilities of the OH, OH$^+$, and OH$^-$ systems. The OH molecule was chosen because it possesses stable positive and negative anions, whose electronic polarizabilities have been studied by several workers.[16,17] The present research is the first to address the nuclear polarizability and hyperpolarizability of an anionic system. We shall see how differently the nuclear motion of a diatomic molecule responds to the external electric field when the molecule attaches an additional electron, loses an electron, or remains neutral.

II. METHODOLOGY

In the Born–Oppenheimer approximation, the wave function of the Schrödinger equation for all particles is assumed to be a product of the electronic and nuclear component $\Psi_e(\bar{r}_i;\bar{R}_\alpha)\Psi_n(\bar{R}_\alpha)$, where the electronic wave function depends explicitly on the electronic coordinates $\bar{r}_i$ and parametrically on the location of the nuclei, $\bar{R}_\alpha$. Inserting this into the Schrödinger equation, we find that upon neglecting the $(\hbar^2/2m_\alpha)\nabla_\alpha\Psi_e\nabla_\alpha\Psi_n$ and $(\hbar^2/2m_\alpha)\Psi_n\nabla^2_\alpha\Psi_e$ terms, we can separately solve for $\Psi_e(\bar{r}_i;\bar{R}_\alpha)$, by fixing much heavier nuclei. Using the electron energy $W_e(\bar{R}_\alpha)$ as the potential for the nuclei, we then solve the equation for the nuclear motion. The electronic and nuclear equations for a system exposed to an external electronic field, directed along the z axis, are as follows:

$$[T_e + V(\bar{r}_i;\bar{R}_\alpha) + F_z\mu(r_{zi})]\Psi_e(\bar{r}_i;\bar{R}_\alpha,F_z)$$
$$= W(\bar{R}_\alpha;F_z)\Psi_e(\bar{r}_i;\bar{R}_\alpha,F_z), \qquad (4a)$$
$$[T_n + W_e(\bar{R}_\alpha;F_z)]\Psi_n(\bar{R}_\alpha;F_z)$$
$$= W(F_z)\Psi(\bar{R}_\alpha;F_z). \qquad (4b)$$

T_e and T_n are the kinetic energy operators for electrons and nuclei, respectively, and $V(\bar{r}_i;\bar{R}_\alpha)$ is the electrostatic potential between all pairs of particles. The $F_z\mu(r_{zi})$ operator represents the interaction between the electrons and the external electric field. The origin of the coordinate system is positioned in the center of the molecular nuclear charge, therefore eliminating the field–nuclei interaction.

In the present study we limit our consideration to diatomic systems and to the external electric field directed along the molecular axis. As pointed out by Epstein,[18] Bishop and Solunac,[9] and Brieger,[19] this creates a physically artificial situation in the sense that the actual Stark Hamiltonian should be related to a laboratory coordinate system rather than to an internal molecular one as recently formulated by Bishop and Lam.[20] However, the purpose of the present calculations is to provide benchmark results of the parallel components of the polarizability, first and second hyperpolarizabilities, which can be utilized in a future study with a laboratory-fixed Stark Hamiltonian.

The total molecular energy is calculated for five different magnitudes of the electric field including the field-free case, distributed as: $-2F_z, -F_z, 0, +F_z, +2F_z$. The molecular dipole moment (μ_z), parallel molecular polarizability (α_{zz}), first and second hyperpolarizabilities $(\beta_{zzz}, \gamma_{zzzz})$

are determined by numerical differentiation of the total energy with respect to the field strength. The appropriate formulas are formally identical as for the electronic polarizabilities.[4]

Multiple numerical differentiation requires an adequate size of the field strengths to ensure that significant energy differences are obtained. In this work, field strengths of 0.0, ± 0.01, and ± 0.02 are found suitable for the OH molecule and OH$^+$ cation; however, the field strengths have to be reduced to ± 0.001 and ± 0.002 for the OH$^-$ anion due to problems with the stability of the electronic calculation.

The solution of the electronic equation has been accomplished with the numerical MCSCF procedure.[21] The same method has been used before by Christiansen and McCullough[22,23] and by us[4] to determine polarizabilities for the FH molecule. Numerical MCSCF technique utilizes partial wave expansions in elliptical coordinates for molecular orbitals. The one-dimensional numerical component in this expansion is determined by solving an integro-differential Fock equation on a grid of exponentially distributed points. The Fock operator includes interaction with the external electric field. The result of the numerical MCSCF procedure is an essentially exact MCSCF wave function for a given configuration list. In the present calculations we use the restricted Hartree–Fock single-determinantal approximation which for the systems studied relates to the following electronic configurations:

OH$^+$: $(1\sigma)^2$　$(2\sigma)^2$　$(3\sigma)^2$　$(\pi_{-1})^1$　$(\pi_{+1})^1$　$^3\Sigma$;

OH　: $(1\sigma)^2$　$(2\sigma)^2$　$(3\sigma)^2$　$(\pi_{-1})^2$　$(\pi_{+1})^1$　$^2\Pi$;

OH$^-$: $(1\sigma)^2$　$(2\sigma)^2$　$(3\sigma)^2$　$(\pi_{-1})^2$　$(\pi_{-1})^2$　$^1\Sigma$.

The electronic energy has been calculated for field-free and field dependent cases in 63 points densely spaced between 1.2 and 3.5 a.u. One exception is the OH molecule for which convergence difficulties in the numerical Hartree–Fock calculations with the electric field did not allow us to go beyond 3.0 a.u.

The energy functions were used to evaluate the first three vibrational levels for OH, the first five levels for OH$^+$, and the first six levels for OH$^-$ with plausible accuracy. The molecular vibrational equation has been solved numerically using the program DVIBRO originally created by Kirby-Docken and Hinze.[24]

III. RESULTS

Structural information presented in Table I shows the degree that the equilibrium internuclear distance changes for the OH, OH$^+$, and OH$^-$ systems subject to an electric field. When the field alters direction from -0.02 to $+0.02$ a.u. (the bond axis orientation is from oxygen to hydrogen), the nuclear separation lengthens by 0.0118 a.u. for OH and almost five times that much for OH$^+$ (0.0510 a.u.). In contrast, for the OH$^-$ anion, a switch of the field from -0.002 to $+0.002$ causes the bond to shrink by 0.0011 a.u.

In Table I we also present the total electronic energies obtained for the field-free equilibrium geometries with different electric field strengths. The ten-digit accuracy of the results reflects a very tight convergence criterium imposed

TABLE I. Energies and equilibrium internuclear distances for the OH, OH$^+$, and OH$^-$ systems calculated with the numerical Hartree–Fock method for various magnitudes in the external electric field parallel to the molecular axis. In atomic units.

		Electric field (a.u.)				
		-0.02	-0.01	0.0	$+0.01$	$+0.02$
OH						
	R_{eq}:	1.7911	1.7922	1.7946	1.7981	1.8029
	Energy($R = 1.7946$):	$-75.409\ 565\ 86$	$-75.415\ 267\ 61$	$-75.421\ 738\ 73$	$-75.428\ 964\ 46$	$-75.436\ 935\ 88$
OH$^+$						
	R_{eq}:	1.8764	1.8867	1.8982	1.9117	1.9274
	Energy($R = 1.8982$):	$-74.987\ 262\ 95$	$-74.994\ 675\ 95$	$-75.002\ 546\ 93$	$-75.010\ 867\ 74$	$-75.019\ 631\ 52$
		-0.002	-0.001	0.0	$+0.001$	$+0.002$
OH$^-$						
	R_{eq}:	1.7811	1.7808	1.7805	1.7803	1.7800
	Energy($R = 1.7805$):	$-75.417\ 658\ 56$	$-75.418\ 221\ 95$	$-75.418\ 803\ 71$	$-75.419\ 403\ 82$	$-75.420\ 022\ 23$

on the numerical wave function in the calculations rather than the absolute accuracy, which we estimate to be not more than eight to nine digits.

Table II presents vibrational levels calculated for different magnitudes of the external electric field. Again, we see an inconsistent behavior of the systems studied, with OH$^-$ being an exception. A minus–plus alternation of the field causes the vibrational frequencies to decrease for OH and OH$^+$, and to increase for OH$^-$. This decrease between field strength of -0.02 and $+0.02$ a.u. amounts to only 74 cm^{-1} for the OH $v = 0,1$ transition, and for as much as 313 cm^{-1} for OH$^+$ $v = 0,1$ transition. The appropriate decrease for the $v = 1,2$ transition is 72 cm^{-1} for OH and 497 cm^{-1} for OH$^+$. For the OH$^-$ anion, the increase of the transition

TABLE II. Energies for the first few vibrational levels of the OH, OH$^+$, and OH$^-$ systems calculated with the numerical Hartree–Fock method for various magnitudes of the external electric field parallel to the molecular axis. Numbers in parentheses indicate relative energy separations between consecutive vibrational levels, in cm^{-1}.

		-0.02	-0.01	0.0	$+0.01$	$+0.02$
OH						
	$v = 0$	$-75.400\ 367\ 07$ (3921)	$-75.406\ 067\ 28$ (3922)	$-75.412\ 565\ 43$ (3910)	$-75.419\ 850\ 28$ (3885)	$-75.427\ 919\ 64$ (3847)
	$v = 1$	$-75.382\ 503\ 63$ (3775)	$-75.388\ 197\ 99$ (3778)	$-75.394\ 751\ 69$ (3767)	$-75.402\ 150\ 19$ (3742)	$-75.410\ 390\ 02$ (3703)
	$v = 2$	$-75.365\ 304\ 37$	$-75.370\ 982\ 29$	$-75.377\ 587\ 09$	$-75.385\ 100\ 40$	$-75.393\ 517\ 35$
OH$^+$						
	$v = 0$	$-74.979\ 325\ 79$ (3416)	$-74.986\ 840\ 17$ (3334)	$-74.994\ 885\ 11$ (3239)	$-75.003\ 474\ 50$ (3129)	$-75.012\ 628\ 20$ (3003)
	$v = 1$	$-74.963\ 760\ 93$ (3275)	$-74.971\ 650\ 35$ (3186)	$-74.980\ 129\ 14$ (3082)	$-74.989\ 218\ 14$ (2962)	$-74.998\ 947\ 51$ (2822)
	$v = 2$	$-74.948\ 840\ 62$ (3138)	$-74.957\ 134\ 72$ (3042)	$-74.966\ 085\ 15$ (2930)	$-74.975\ 722\ 36$ (2798)	$-74.986\ 091\ 35$ (2641)
	$v = 3$	$-74.934\ 542\ 82$ (3006)	$-74.943\ 273\ 12$ (2903)	$-74.952\ 736\ 11$ (2781)	$-74.962\ 975\ 48$ (2635)	$-74.974\ 057\ 63$ (2460)
	$v = 4$	$-74.920\ 846\ 31$	$-74.930\ 046\ 29$	$-74.940\ 066\ 15$	$-74.950\ 967\ 84$	$-74.962\ 848\ 84$
		-0.002	-0.001	0.0	$+0.001$	$+0.002$
OH$^-$						
	$v = 0$	$-75.408\ 505\ 79$ (3873)	$-75.409\ 056\ 63$ (3880)	$-75.409\ 626\ 47$ (3886)	$-75.410\ 215\ 26$ (3892)	$-75.410\ 822\ 94$ (3897)
	$v = 1$	$-75.390\ 857\ 68$ (3687)	$-75.391\ 379\ 07$ (3695)	$-75.391\ 920\ 78$ (3702)	$-75.392\ 482\ 73$ (3710)	$-75.393\ 064\ 85$ (3717)
	$v = 2$	$-75.374\ 060\ 68$ (3500)	$-75.374\ 545\ 19$ (3510)	$-75.375\ 051\ 67$ (3520)	$-75.375\ 579\ 96$ (3529)	$-75.376\ 129\ 98$ (3538)
	$v = 3$	$-75.358\ 111\ 27$ (3315)	$-75.358\ 550\ 40$ (3327)	$-75.359\ 013\ 51$ (3339)	$-75.359\ 500\ 39$ (3350)	$-75.360\ 010\ 87$ (3360)
	$v = 4$	$-75.343\ 005\ 22$ (3132)	$-75.343\ 389\ 39$ (3146)	$-75.343\ 800\ 00$ (3160)	$-75.344\ 236\ 74$ (3173)	$-75.344\ 699\ 37$ (3185)
	$v = 5$	$-75.328\ 736\ 99$	$-75.329\ 055\ 55$	$-75.329\ 403\ 54$	$-75.329\ 780\ 51$	$-75.330\ 186\ 10$

frequency for the $-0.002-+0.002$ field switch equals to 24 cm^{-1} for the $v = 0,1$ transition and rises to 53 cm^{-1} for the $v = 4,5$ transition.

In Table III, the internuclear distance average over different vibrational levels is shown. One may draw two conclusions upon examining these results. First, there is an obvious steady increase of the distance with the level of the vibrational excitation, which for OH and OH⁻ remains almost the same, regardless of the direction and size of the electric field, but for OH⁺ the increase is noticeably larger for the positive values of the electric field than it is for the negative values. A vibrationally excited OH molecule from $v = 0$ to $v = 1$ changes its internuclear distance by 0.1164 when exposed to an electric field of -0.02 a.u. and by 0.1180 for a field of $+0.02$ a.u.; for OH⁺, the appropriate changes are 0.1316 and 0.1646 a.u. Second, the vibrationally averaged internuclear separation increases when the field rises from negative to positive values for OH (by 0.0121 a.u.) and for OH⁺ (by 0.0572 a.u.), but decreases for OH⁻ (by 0.0015 a.u.). However, the increase is almost not affected by a vibrational excitation from $v = 0$ to $v = 2$ in the case of OH, but for OH⁺ it rises from 0.0572 a.u. to 0.0902 a.u. For OH⁻ the decrease of the internuclear separation is very sensitive to a vibrational excitation and changes from 0.0015 a.u. for $v = 0$ to 0.0040 for $v = 2$.

Finally, Tables IV and V contain our results for the dipole moment, polarizability and first and second hyperpolarizabilities. In the first table we present vibrationally averaged electronic results, as well as the results calculated for the equilibrium geometries from Table I. In Table II, there are results obtained by numerical differentiation of the total molecular energy (electronic + vibrational). For the OH⁻

TABLE IV. Vibrationally averaged dipole moment (μ_z), polarizability (α_{zz}), and first and second hyperpolarizabilities ($\beta_{zzz}, \gamma_{zzzz}$) for OH, OH⁺, and OH⁻. In atomic units.

		μ_z	α_{zz}	β_{zzz}	γ_{zzzz}
OH					
	$R = 1.7946$	0.6850	7.541	-11.83	582
	$v = 0$	0.6893	7.809	-13.43	630
	$v = 1$	0.6978	8.386	-16.97	723
	$v = 2$	0.7061	9.020	-20.98	826
OH⁺					
	$R = 1.8982$	0.8097	4.497	-7.511	128
	$v = 0$	0.8314	4.679	-8.61	139
	$v = 1$	0.8780	5.067	-11.13	165
	$v = 2$	0.9288	5.488	-14.16	194
	$v = 3$	0.9842	5.944	-17.81	228
	$v = 4$	1.0448	6.437	-22.22	267
OH⁻					
	$R = 1.7805$	0.5909	18.34	(-32)	
	$v = 0$	0.5793	18.85	(-35)	
	$v = 1$	0.5518	20.03	(-46)	
	$v = 2$	0.5174	21.42	(-64)	
	$v = 3$	0.4750	23.04	(-88)	
	$v = 4$	0.4237	24.93	(-120)	
	$v = 5$	0.3625	27.08	(-157)	

anion only, μ_z and α_{zz} could be calculated with adequate accuracy due to small values of the electric field used. We, however, show the values of β_{zzz} in parenthesis with the hope that at least the first digits in the results are correct.

The following conclusions can be drawn by examining the results:

(1) The vibrationally averaged dipole moment is identical with the result obtained by the numerical differentiation of the appropriate vibrational energies with respect to the

TABLE III. Vibrationally averaged internuclear distances for the OH, OH⁺, and OH⁻ systems for different strengths of the external electric field parallel to the molecular axis. In atomic units.

		Electric field (a.u.)				
		-0.02	-0.01	0.0	$+0.01$	$+0.02$
OH						
	$v = 0$	1.8190	1.8200	1.8223	1.8260	1.8311
	$v = 1$	1.8765	1.8772	1.8796	1.8836	1.8894
	$v = 2$	1.9354	1.9356	1.9381	1.9425	1.9491
OH⁺						
	$v = 0$	1.9080	1.9192	1.9322	1.9474	1.9652
	$v = 1$	1.9729	1.9865	2.0027	2.0219	2.0449
	$v = 2$	2.0396	2.0561	2.0761	2.1002	2.1298
	$v = 3$	2.1081	2.1281	2.1525	2.1827	2.2209
	$v = 4$	2.1786	2.2026	2.2325	2.2702	2.3195
		-0.002	-0.001	0.0	$+0.001$	$+0.002$
OH⁻						
	$v = 0$	1.8111	1.8107	1.8103	1.8099	1.8096
	$v = 1$	1.8738	1.8731	1.8724	1.8718	1.8712
	$v = 2$	1.9397	1.9386	1.9376	1.9366	1.9357
	$v = 3$	2.0093	2.0077	2.0063	2.0049	2.0036
	$v = 4$	2.0831	2.0809	2.0789	2.0769	2.0751
	$v = 5$	2.1617	2.1587	2.1559	2.1532	2.1507

TABLE V. Total molecular parallel polarizabilities (α_{zz}) and hyperpolarizabilities ($\beta_{zzz}, \gamma_{zzzz}$) for the first few vibrational levels of the OH, OH⁺, and OH⁻ systems. In atomic units.

		μ_z	α_{zz}	β_{zzz}	γ_{zzzz}
OH					
	$v = 0$	0.6893	7.859	-6.72	905
	$v = 1$	0.6978	8.439	-9.01	1107
	$v = 2$	0.7061	9.074	-11.62	1350
OH⁺					
	$v = 0$	0.8314	5.440	16.88	597
	$v = 1$	0.8780	6.094	25.50	932
	$v = 2$	0.9288	6.856	37.73	1455
	$v = 3$	0.4842	7.745	55.05	2271
	$v = 4$	1.0448	8.789	79.72	3553
OH⁻					
	$v = 0$	0.5793	18.95	(-55)	
	$v = 1$	0.5518	20.24	(-75)	
	$v = 2$	0.5174	21.80	(-120)	
	$v = 3$	0.4750	23.77	(-190)	
	$v = 4$	0.4237	26.12	(-275)	
	$v = 5$	0.3626	28.97	(-405)	

field strength. This, obviously, must happen because the only vibrational contribution to the molecular permanent dipole moment originates only from averaging the dipole moment calculated for different internuclear separations over the vibrational state of the molecule.

(2) The electronic polarizabilities for OH and OH⁻ averaged over vibrational levels differ very little from the total molecular polarizabilities of Table V. In both cases, the polarizability calculated for $v = 0$ is 3%–4% higher than the result obtained at the Hartree–Fock equilibrium geometry. For $v = 2$, the increase is 20% for OH and 17%–19% for OH⁻. The situation is quite different for OH⁺. The averaged α_{zz} for $v = 0$ is only 4% above the polarizability at the equilibrium, while the total molecular α_{zz} exceeds this result by 21%. For $v = 2$, the appropriate percentiles are 22% and 52%.

(3) The vibronic contribution to the first hyperpolarizability β_{zzz} is much more pronounced, and the vibrationally averaged result differs significantly from the total molecular hyperpolarizabilities of Table V. For all three systems the vibrational averaging makes the value of β_{zzz} more negative in comparison with the value of β_{zzz} at the equilibrium geometry. This trend is, however, reversed for OH and OH⁺ results of the total molecular hyperpolarizability. The values of β_{zzz} for OH at the equilibrium geometry, vibrationally averaged ($v = 0$) and total are: − 11.83, − 13.43, and − 6.72 a.u., respectively. For OH⁺ we observe even more dramatic differences, and the appropriate results are: − 7.511, − 8.614, and + 16.88 (!) a.u. The OH⁻ hyperpolarizabilities are consistently negative, and the similar comparison is as follows: − 32 a.u. (equilibrium), − 35 a.u. (averaged for $v = 0$) and − 55 (total for $v = 0$).

(4) The second hyperpolarizabilities have been calculated only for OH and OH⁺. The vibrational averaging does not alter the result obtained at the equilibrium geometry for either of the molecules. However, the total molecular results of Table V are significantly different from the vibrational averages and this trend intensifies for higher vibrational levels. For the ground state vibration, the total molecular γ_{zzzz} of OH is by almost one-half higher than the vibrationally averaged result, while for OH⁺ the appropriate factor equals as much as 4.3.

IV. SUMMARY

The vibrational contributions to molecular parallel polarizabilities and first and second hyperpolarizabilities have been analyzed for three diatomic systems with the same nuclei but a different number of electrons, making one of them an anion, the second a cation, and the third a neutral system. The present study suggests that it is necessary to account for the distortion of the nuclear frame simultaneously with the electronic deformation to accurately determine the molecular response to the external static electric field. These might be important when considering nonlinear optical phenomena that are generated when using a static field.

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