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Vibrational corrections to hyperpolarizabilities of the O₃, SO₂, N₂O and CO₂ molecules: A comparison between variational and perturbation methods

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ABSTRACT

In this work we reported results of vibrational corrections to the first and second hyperpolarizabilities of the O₃, SO₂, N₂O and CO₂ molecules at the CCSD level through the BKPT method of Bishop and Kirtman and also using a variational approximation proposed in a previous work. Comparison between results obtained by both methods shows that the performance of BKPT is different for the systems studied here. Practically the same results are obtained for sulfur dioxide while ozone is the system for which there is greater discrepancy between the results obtained by the two procedures.

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1. Introduction

Nonlinear optics has gained a prominent role in nowadays because of the number applications of this science in important fields as optical computers, communications and medicine [1,2]. Along with this, there is great interest in the computation of hyperpolarizabilities, which are the quantities related to the nonlinear optical processes in molecular level. Although theoretical results are recognized as valuable data for comparison with experiment, the *ab initio* prediction of hyperpolarizabilities is a challenge, since it requires the use of extensive basis sets and the proper handling of important effects as electron correlation and vibrational corrections [3–8]. With the exception of a few nonadiabatic calculations for diatomic molecules [9,10], the Born–Oppenheimer approximation is generally invoked as a starting point for computation of molecular electric properties. In this context, the total hyperpolarizability is frequently obtained in two steps: initially one calculates the electronic contribution on the equilibrium geometry, neglecting the nuclear motion effects; in the sequence is made a correction, called vibrational correction, with the purpose of including these effects [11].

Significant advances for calculations of the electronic part have been obtained with response theories that permit the simultaneous inclusion of both electron correlation and frequency dispersion effects. Linear, quadratic and cubic response theories based on

coupled cluster wave functions allow the computation of dynamic hyperpolarizabilities at high level of electron correlation [12–14].

The recognition of the import role played by the vibrational corrections in calculations of molecular electrical properties is directly linked to the Bishop and Kirtman's work. Two decades ago they presented a perturbation treatment (BKPT) that became the reference methodology for computing static and dynamic vibrational electric properties of polyatomic molecules [15,16]. The core of the approach is the expansion of the potential energy and electronic properties in terms of the vibrational normal coordinates, which leads to compact formulas (expressed in terms of the harmonic vibrational frequencies and derivatives of the energy and electronic properties with respect to the normal coordinates) to calculate the vibrational hyperpolarizabilities [11,15–17]. Bishop, Kirtman and coworkers also developed an alternative methodology based on the finite field-nuclear relaxation (FF-NR) [18,19]. Although both methods lead to the same results if all terms are included, they divide the total vibrational hyperpolarizability in different ways. While in the BKPT method the property p ($p = \beta$ or γ) is divided in zero-point vibrational averaging (p^{ZPVA}) and pure vibrational (p^{PV}) corrections, in the FF-NR method p is partitioned in nuclear relaxation (p^{NR}) and curvature (p^{C}) contributions [11]. Whether the field-dependent vibrational energies and wave functions are calculated using modern approaches the FF-NR method is able to provide reliable results even for highly anharmonic systems, for which the perturbation approach is not suitable [8,20,21]. Combined electronic and vibrational response functions have been presented by Christiansen and coworkers. Linear, quadratic and cubic response functions were derived and

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implemented for vibrational self-consistent field (VSCF) and vibrational configuration interaction (VCI) vibrational wave functions, allowing analytical calculations of the vibrational dynamic polarizability and hyperpolarizabilities [22–25]. It was shown that the total response includes terms not present in the BKPT treatment, called mixed terms, and that these terms disappear in the static limit [24]. Kirtman and Luis showed that the mixed terms also vanish in the high-frequency limit [26]. Recently we have proposed a variational approach (VAR) to compute vibrational (hyper)polarizabilities that have been applied to the lithium salt of pyridazine molecule [27]. Results obtained showed that the variational approach is able to fix partly the deficiencies of the BKPT method for calculating the vibrational first hyperpolarizability.

In this Letter we present a comparison between the results obtained through the BKPT and VAR methods for the vibrational first and second hyperpolarizabilities of the O₃, SO₂, N₂O and CO₂ triatomic molecules. A reason for choosing these systems is that the small number of normal modes allows us to make a more detailed description of the vibrational problem at high level of electron correlation. A question that we address is the convergence of the variational results as the basis set of harmonic vibrational wave functions is expanded. Our results show that there can be significant differences in performance of the methodologies for the systems studied here. Our focus is placed on the pv correction since the zpva correction is in general small for all systems studied. The hyperpolarizabilities reported in this work are $\beta(-2\omega; \omega, \omega)$, $\gamma(-\omega; \omega, \omega, -\omega)$ and $\gamma(-\omega; \omega, 0, 0)$. They are associated to the second harmonic generation (SHG), intensity dependent refractive index (IDRI), and dc-Kerr effect (dc-K) nonlinear optical processes, respectively. It should be stressed that BKPT results for O₃ and SO₂ have been previously published [28,29]. Other results have also been published for the carbon dioxide and nitrous oxide molecules, but at lower levels of electron correlation. Bishop et al. [30] reported results for the vibrational second hyperpolarizability of CO₂ at the self-consistent field (SCF) and Möller–Plesset perturbation theory (MP2) levels by applying the BKPT method, while Andrés et al. [31] calculated the first and second hyperpolarizabilities of N₂O at the SCF level through the FF-NR method.

2. Theory

In this work we have adopted the partition of the vibrational contribution in zero-point vibrational average (zpva) and pure vibrational (pv) corrections [11]. The zpva correction is the difference between the average of the corresponding electronic contribution, calculated using the zero-point vibrational wave function, and the electronic value of the property computed on the equilibrium geometry. The pv corrections for the first and second hyperpolarizabilities are usually written as $\beta^{pv} = [\mu\alpha] + [\mu^3]$ and $\gamma^{pv} = [\alpha^2] + [\mu\beta] + [\mu^2\alpha] + [\mu^4]$. The results obtained in this work by means of the BKPT method include terms up to first general (electrical + mechanical) order of perturbation, such that the hyperpolarizabilities are given by $\beta^{pv} = [\mu\alpha]^{0,0} + [\mu^3]^{1,0} + [\mu^3]^{0,1}$ and $\gamma^{pv} = [\alpha^2]^{0,0} + [\mu\beta]^{0,0} + [\mu^2\alpha]^{1,0} + [\mu^2\alpha]^{0,1}$. All the expressions for the square brackets appearing in the above expressions are provided elsewhere [11,15–17,28,29].

The variational approach used here is based in the diagonalization of the *M*-modes vibrational Hamiltonian in the basis of *M*-modes vibrational wave functions that are product of single-mode harmonic oscillator functions. The procedure to calculate the matrix elements of the vibrational Hamiltonian and to compute the matrix elements of the properties that appear in the expressions for the square brackets were presented in the previous work [27]. The potential energy was expanded as a power series in

the normal coordinates up to third order and the properties were expanded up to second order.

The electronic properties were computed analytically by means of coupled cluster linear, quadratic and cubic response theories [12–14] at the CCSD level with d-aug-cc-pVTZ basis sets by means of the DALTON program [32]. This basis sets has been shown suitable to compute hyperpolarizabilities of the O₃ and SO₂ [28,29].

3. Results and discussion

Initially we performed geometry optimizations and frequency calculations for all systems studied here at the CCSD level with d-aug-cc-pVTZ basis sets through GAUSSIAN 09 program [33]. Table 1 shows the optimized bond lengths and angles and the vibrational frequencies calculated along with experimental values collected from literature [34–40]. Results for O₃ and SO₂ were previously reported [28,29] and are included for easy comparison. It can be observed that in general the CCSD method yields results in good agreement with the experiment. This accordance is important because the vibrational frequencies and normal coordinates, which are computed at the equilibrium geometry, play a central role in our calculations of vibrational hyperpolarizabilities. For the bond length, the largest discrepancy occurs in the case of the ozone molecule, for which the CCSD value is 0.023 Å smaller than the experimental one. For the other systems the differences are much smaller. The calculated bond angle is only 0.9° larger (smaller) than the experimental result for the ozone (sulfur dioxide). The CCSD vibrational frequencies are somewhat higher than the experimental counterparts and the most relevant discrepancy also happen for the ozone: 6%, 12% and 15% for the bending, symmetric stretching and asymmetric stretching modes, respectively. For the other systems, the difference does not reach 6%.

CCSD/d-aug-cc-pVTZ results for the electronic and vibrational first hyperpolarizabilities of O₃, SO₂, and N₂O are presented in Table 2 for the frequencies 0, 0.0010, 0.0239, 0.0428, and 0.0656 hartree. For simplicity, only the values of the $\bar{\beta}$ isotropic quantity [see definition in Ref. 11] are reported. BKPT results for O₃ and SO₂ have been previously published [28,29] and are displayed for comparison. Table 2 has two columns associated to the VAR method for each term. The number to the right of the square bracket in the variational results indicates the maximum value of the sum of single-mode quantum numbers in the *M*-modes wave functions. In order to make a more appropriate comparison between the BKPT and VAR methodologies, we have taken this value equal to 3, so that the basis of harmonic oscillator functions contains all vibrational functions that contribute in BKPT up to first general order of perturbation. On the other hand, the maximum value 6 ensures converged variational results for all terms, for all systems. Regarding the term $[\mu\alpha]$, one can see that BKPT and VAR results are practically identical for the sulfur dioxide, for all frequencies quoted, but somewhat different for the ozone and nitrous oxide molecules. At the static limit, the BKPT value is 13% larger (9% smaller) than the VAR result for ozone (nitrous oxide). In the case of ozone, the differences are larger for higher frequencies. The very small differences between the $[\mu\alpha]_3$ and $[\mu\alpha]_6$ results, for all systems, shows that the converged variational result for this term can be achieved including only the *M*-modes vibrational basis functions that appear in BKPT up to first general order of perturbation.

The comparison for the term $[\mu^3]$ must take into account that in BKPT it is written as $[\mu^3]^{1,0} + [\mu^3]^{0,1}$, while in the variational approach there is a unique contribution. We stress that although the terms $[\mu^3]$ are relatively small compared to the electronic counterparts, the goal here is to compare the performance of the methodologies. An initial observation concerns to the signs of the

Table 1
Geometric parameters (in Å and degrees) and vibrational frequencies (in cm^{-1}) of the O_3 , SO_2 , N_2O and CO_2 triatomic molecules calculated at the CCSD level with the d-aug-cc-pVTZ basis set. Experimental values are also displayed for comparison. For the N_2O , the first and second numbers refer to N–N and N–O bonds, respectively.

	Bond length		Angle		Bending		Sym. stretching		Asym. stretching	
	CCSD	Expt.	CCSD	Expt.	CCSD	Expt.	CCSD	Expt.	CCSD	Expt.
O_3	1.249	1.272 ^a	117.7	116.8 ^a	761	716 ^b	1273	1135 ^b	1255	1089 ^b
SO_2	1.441	1.431 ^c	118.4	119.3 ^c	531	518 ^d	1206	1151 ^d	1399	1362 ^d
CO_2	1.160	1.160 ^e			690	673 ^f	1386	1353 ^f	2415	2393 ^f
N_2O	1.119	1.127 ^g			617	589 ^g	1319	1285 ^g	2351	2224 ^g
	1.186	1.186 ^g								

^a Ref. [34].

^b Ref. [35].

^c Ref. [36].

^d Ref. [37].

^e Ref. [38].

^f Ref. [39].

^g Ref. [40].

Table 2
Pure vibrational corrections to the dynamic first hyperpolarizabilities related to the second harmonic generation of the O_3 , SO_2 , and N_2O molecules calculated at the CCSD level with the d-aug-cc-pVTZ basis set (in atomic units). The number to the right of the square-bracket in the variational results indicates the maximum value of the sum of single-mode quantum numbers in the M -modes wave functions.

	ω	el	BKPT			VAR			
			$[\mu\alpha]^{0,0}$	$[\mu^3]^{0,1}$	$[\mu^3]^{0,1}$	$[\mu\alpha]3$	$[\mu\alpha]6$	$[\mu^3]3$	$[\mu^3]6$
O_3	0	16.51	14.51	2.84	-2.15	12.88	12.94	0.90	0.71
	0.0010	16.51	14.72	3.16	-2.95	12.92	12.94	0.42	0.08
	0.0239	17.32	-0.80	0.01	0	-0.59	-0.58	0.01	0.01
	0.0428	19.92	-0.24	0	0	-0.18	-0.18	0	0
	0.0656	24.94	-0.10	0	0	-0.08	-0.08	0	0
SO_2	0	35.95	56.59	-3.52	-0.36	56.58	56.58	-3.87	-3.88
	0.0010	35.95	68.69	-1.86	-2.94	68.66	68.67	-4.79	-4.79
	0.0239	36.81	-2.30	0	0	-2.30	-2.30	0	0
	0.0428	38.93	-0.69	0	0	-0.69	-0.69	0	0
	0.0656	44.82	-0.29	0	0	-0.29	-0.29	0	0
N_2O	0	45.12	18.52	-11.42	15.94	20.28	20.78	4.31	6.25
	0.0010	45.13	20.36	-10.59	18.21	22.41	23.01	7.33	9.77
	0.0239	45.97	2.26	-0.13	0	2.17	2.18	-0.11	-0.13
	0.0428	47.92	0.54	-0.01	0	0.52	0.52	-0.01	-0.01
	0.0656	52.18	0.22	0	0	0.21	0.21	0	0

terms $[\mu^3]^{1,0}$ and $[\mu^3]^{0,1}$ which are equal in the case of SO_2 and opposite for O_3 and N_2O . For the sulfur dioxide, the sum $[\mu^3]^{1,0} + [\mu^3]^{0,1}$ is practically equal to the VAR result, showing the excellent performance of the BKPT method. Furthermore there is practically no difference between the $[\mu^3]3$ and $[\mu^3]6$ results. In the case of the nitrous oxide, the sum $[\mu^3]^{1,0} + [\mu^3]^{0,1}$ is only 5% larger than the $[\mu^3]3$ result at the static limit. The comparison

between the variational results shows that the $[\mu^3]3$ result is around 30% smaller than the $[\mu^3]6$ converged value at this limit. For the ozone, at the static limit, the BKPT result is 23% smaller than the $[\mu^3]3$ value and almost coincident with the $[\mu^3]6$ result. In BKPT, the part of the term $[\mu^3]$ that cannot be added without inclusion of anharmonicity in the potential appears in the lowest order of perturbation (first-order). Unlike, for the term $[\mu\alpha]$, the

Table 3
Pure vibrational corrections to the dynamic second hyperpolarizability of the O_3 molecule calculated at the CCSD level with the d-aug-cc-pVTZ basis set (in atomic units). The number to the right of the square-bracket in the variational results indicates the maximum value of the sum of single-mode quantum numbers in the M -modes wave functions.

ω	el	BKPT				VAR					
		$[\alpha^2]^{0,0}$	$[\mu\beta]^{0,0}$	$[\mu^2\alpha]^{1,0}$	$[\mu^2\alpha]^{0,1}$	$[\alpha^2]3$	$[\alpha^2]6$	$[\mu\beta]3$	$[\mu\beta]6$	$[\mu^2\alpha]3$	$[\mu^2\alpha]6$
Static											
0	1857	217	666	650	77	3295	3498	707	721	1031	1562
IDRI											
0.0010	1857	247	685	696	98	3392	3607	729	744	1165	1759
0.0239	1889	144	-43	0	0	2146	2280	-42	-41	15	16
0.0428	1970	145	-13	0	0	2181	2317	-12	-12	4	4
0.0656	2138	145	-5	0	0	2190	2326	-5	-5	1	1
dc-K											
0.0010	1857	228	675	672	86	3339	3548	718	733	1096	1659
0.0239	1872	75	322	78	10	332	378	333	340	149	223
0.0428	1907	77	337	95	10	736	787	347	355	157	232
0.0656	1978	78	340	100	10	820	873	351	358	158	235

anharmonicity contributions arise from second-order. Our results show that the treatment of the anharmonicity by means of the BKPT method in first order is suitable for SO₂, but less so for O₃ and N₂O.

The second hyperpolarizabilities of the four systems are presented in Tables 3–6. For simplicity, only the $\bar{\gamma}$ mean values [11] are displayed. Previous BKPT results for O₃ and SO₂ are displayed in these tables for comparison [28,29]. We start the analysis by the term $[\alpha^2]$. It is observed that the results obtained for the term $[\alpha^2]^{0,0}$ are only 5% smaller than the corresponding variational

results for the N₂O and CO₂ molecules for all frequencies considered. For SO₂ the BKPT and VAR results are practically identical. The $[\alpha^2]_3$ and $[\alpha^2]_6$ results are also very close for these three systems. Another fact worth noting is the similarity between the values of this term for N₂O and CO₂. The comparison between BKPT and VAR results is surprisingly different for the O₃ molecule. For this system the values $[\alpha^2]_3$ are more than one order of magnitude larger than the $[\alpha^2]^{0,0}$ counterparts. This large discrepancy does not arise primarily from differences in the BKPT and VAR approaches,

Table 4

Pure vibrational corrections to the dynamic second hyperpolarizability of the SO₂ molecule calculated at the CCSD level with the d-aug-cc-pVTZ basis set (in atomic units). The number to the right of the square-bracket in the variational results indicates the maximum value of the sum of single-mode quantum numbers in the *M*-modes wave functions.

ω	el	BKPT				VAR						
		$[\alpha^2]^{0,0}$	$[\mu\beta]^{0,0}$	$[\mu^2\alpha]^{1,0}$	$[\mu^2\alpha]^{0,1}$	$[\alpha^2]_3$	$[\alpha^2]_6$	$[\mu\beta]_3$	$[\mu\beta]_6$	$[\mu^2\alpha]_3$	$[\mu^2\alpha]_6$	
Static												
0	3309	878	-149	203	41	883	883	-148	-148	258	258	
IDRI												
0.0010	3309	997	-197	332	38	1002	1002	-197	-197	370	370	
0.0239	3376	582	-5	8	0	585	585	-5	-5	3	3	
0.0428	3531	584	-1	2	0	587	587	-1	-1	1	1	
0.0656	3881	585	-1	1	0	588	588	-1	-1	0	0	
dc-K												
0.0010	3309	909	-173	256	41	914	914	-173	-173	330	330	
0.0239	3342	233	-77	21	6	234	234	-77	-77	28	28	
0.0428	3417	255	-75	22	6	257	257	-75	-75	31	31	
0.0656	3571	261	-75	23	6	262	262	-75	-75	31	31	

Table 5

Pure vibrational corrections to the dynamic second hyperpolarizability of the N₂O molecule calculated at the CCSD level with the d-aug-cc-pVTZ basis set (in atomic units). The number to the right of the square-bracket in the variational results indicates the maximum value of the sum of single-mode quantum numbers in the *M*-modes wave functions.

ω	el	BKPT				VAR						
		$[\alpha^2]^{0,0}$	$[\mu\beta]^{0,0}$	$[\mu^2\alpha]^{1,0}$	$[\mu^2\alpha]^{0,1}$	$[\alpha^2]_3$	$[\alpha^2]_6$	$[\mu\beta]_3$	$[\mu\beta]_6$	$[\mu^2\alpha]_3$	$[\mu^2\alpha]_6$	
Static												
0	1787	310	-37	-83	269	326	331	-42	-43	175	214	
IDRI												
0.0010	1787	321	-38	-70	287	339	344	-44	-45	204	248	
0.0239	1818	204	-2	13	7	215	218	-2	-2	12	24	
0.0428	1890	206	0	4	1	217	220	0	0	5	5	
0.0656	2046	206	0	2	0	217	220	0	0	2	2	
dc-K												
0.0010	1787	316	-38	-77	278	333	337	-43	-44	193	234	
0.0239	1803	59	-19	-9	43	62	83	-22	-23	24	38	
0.0428	1838	75	-19	-14	40	79	80	-21	-22	24	30	
0.0656	1909	79	-18	-16	40	83	84	-21	-22	23	28	

Table 6

Pure vibrational corrections to the dynamic second hyperpolarizability of the CO₂ molecule calculated at the CCSD level with the d-aug-cc-pVTZ basis set (in atomic units). The number to the right of the square-bracket in the variational results indicates the maximum value of the sum of single-mode quantum numbers in the *M*-modes wave functions.

ω	el	BKPT				VAR						
		$[\alpha^2]^{0,0}$	$[\mu\beta]^{0,0}$	$[\mu^2\alpha]^{1,0}$	$[\mu^2\alpha]^{0,1}$	$[\alpha^2]_3$	$[\alpha^2]_6$	$[\mu\beta]_3$	$[\mu\beta]_6$	$[\mu^2\alpha]_3$	$[\mu^2\alpha]_6$	
Static												
0	1210	319	-18	277	167	337	340	-19	-19	366	388	
IDRI												
0.0010	1210	331	-18	363	158	349	353	-19	-19	423	448	
0.0239	1226	211	5	11	12	222	225	5	5	10	27	
0.0428	1264	212	1	3	1	224	226	1	1	4	4	
0.0656	1344	213	1	1	0	224	226	1	1	1	2	
dc-K												
0.0010	1210	325	-18	318	163	343	347	-19	-19	404	428	
0.0239	1218	62	-7	20	36	65	66	-7	-7	46	50	
0.0428	1236	75	-8	19	31	79	80	-9	-9	39	42	
0.0656	1274	78	-9	19	30	82	83	-9	-9	37	40	

but from the fact that we have included in the variational approximation the second derivatives of α that do not appear in the term $[\alpha^2]^{0,0}$. A close inspection of equations that define the terms $[\alpha^2]$ and $[\alpha^2]^{0,0}$ [11,15–17] shows that a calculation of $[\alpha^2]$ using harmonic vibrational energies and wave functions with matrix elements including only first derivatives of α leads to the $[\alpha^2]^{0,0}$ result. In order to understand the origin of the large discrepancy in the term $[\alpha^2]$ for ozone, we did a VAR calculation including only first derivatives of α and obtained the result 224 a.u. (at the static limit), which is only 3% larger than the $[\alpha^2]^{0,0}$ value. We also did a calculation using harmonic vibrational energies and wave functions but including first and second derivatives of α and achieved 2506 a.u., making it clear that the major contribution comes from the second derivatives. It is interesting to note that this significant contribution of the second derivatives of α only happens for ozone. A comparison between the variational results for this system shows that in general the $[\alpha^2]_3$ values are approximately 6% smaller than the corresponding $[\alpha^2]_6$ values for all frequencies and both processes considered (except for dc-K at 0.0239 hartree where the difference is larger). In the case of the term $[\mu\beta]$, it can be noted that there are perceptible differences between $[\mu\beta]^{0,0}$ and $[\mu\beta]_3$ only for O_3 and N_2O . Regarding lower frequencies, the BKPT results are around 6% and 14% smaller in magnitude than the VAR results for O_3 and N_2O , respectively. Practically do not exist differences between the $[\mu\beta]_3$ and $[\mu\beta]_6$ results for all systems.

Similar to the case of $[\mu^3]$, the term $[\mu^2\alpha]$ is written in BKPT as $[\mu^2\alpha]^{1,0} + [\mu^2\alpha]^{0,1}$ while in the variational approach these contributions are computed together. It is observed that the terms $[\mu^2\alpha]^{1,0}$ and $[\mu^2\alpha]^{0,1}$ have opposite signs only for N_2O . For the other systems, both terms are positive. For SO_2 , the static BKPT result is only 5% smaller than the $[\mu^2\alpha]_3$ result, which is the converged variational result. For N_2O , the static BKPT result is approximately 6% larger than the $[\mu^2\alpha]_3$ value, which in turn is 18% smaller than the corresponding $[\mu^2\alpha]_6$ converged value. The discrepancies are greater for O_3 and CO_2 molecules. For ozone, the sum $[\mu^2\alpha]^{1,0} + [\mu^2\alpha]^{0,1}$ is around 30% smaller than the $[\mu^2\alpha]_3$ result, which in turn is approximately 30% smaller than the result $[\mu^2\alpha]_6$. For the carbon dioxide, the BKPT values are around 20% larger than the $[\mu^2\alpha]_3$ values for lower frequencies. In this case, the difference between the $[\mu^2\alpha]_3$ and $[\mu^2\alpha]_6$ variational results is around 6%.

The frequency dependence of the hyperpolarizabilities, especially for lower frequencies, can be better illustrated using figures. In order to give the correct physical behavior of the finite lifetimes of the excited states and to prevent hyperpolarizabilities become infinite when ω matches an excitation energy, we introduced a phenomenological dumping factor in the form $\omega_n \rightarrow \omega_n - i\gamma_n$ where γ_n is the inverse of the lifetime of the n th vibrational excited state [23,24,41]. For simplicity we have used the same value $\gamma = 2 \times 10^{-4}$ a.u. for all excited states. This value was chosen to significantly damp the poles without affecting the calculated values of the properties away from them. Figure 1 shows the frequency dependence of the $[\alpha^2]$, $[\mu\beta]$ and $[\mu^2\alpha]$ terms of the second hyperpolarizability of the ozone. Since the curves obtained by different methodologies are visually similar, except at the poles, we display only results of the VAR method with maximum value of the sum of single-mode quantum numbers equal to 6. For the term $[\alpha^2]$ of the dc-K process, one can see three main poles around 0.0027, 0.0055 and 0.0106 hartree. These resonances appear when ω or 2ω matches excitations energies of the 3th, 4th, 9th, and 10th states, whose values are 0.0054, 0.0056, 0.0106 and 0.0107 hartree, respectively. Matrix elements involving these states are in general larger. For the IDRI process only the two first poles are observed because only $(\omega_n - 2\omega)$ or $(\omega_n - 0)$ appear in the denominator of the expression for $[\alpha^2]$ (see Refs. [11,15–17]). For the term $[\mu\beta]$, for both processes, only the pole around 0.0055 hartree is high-

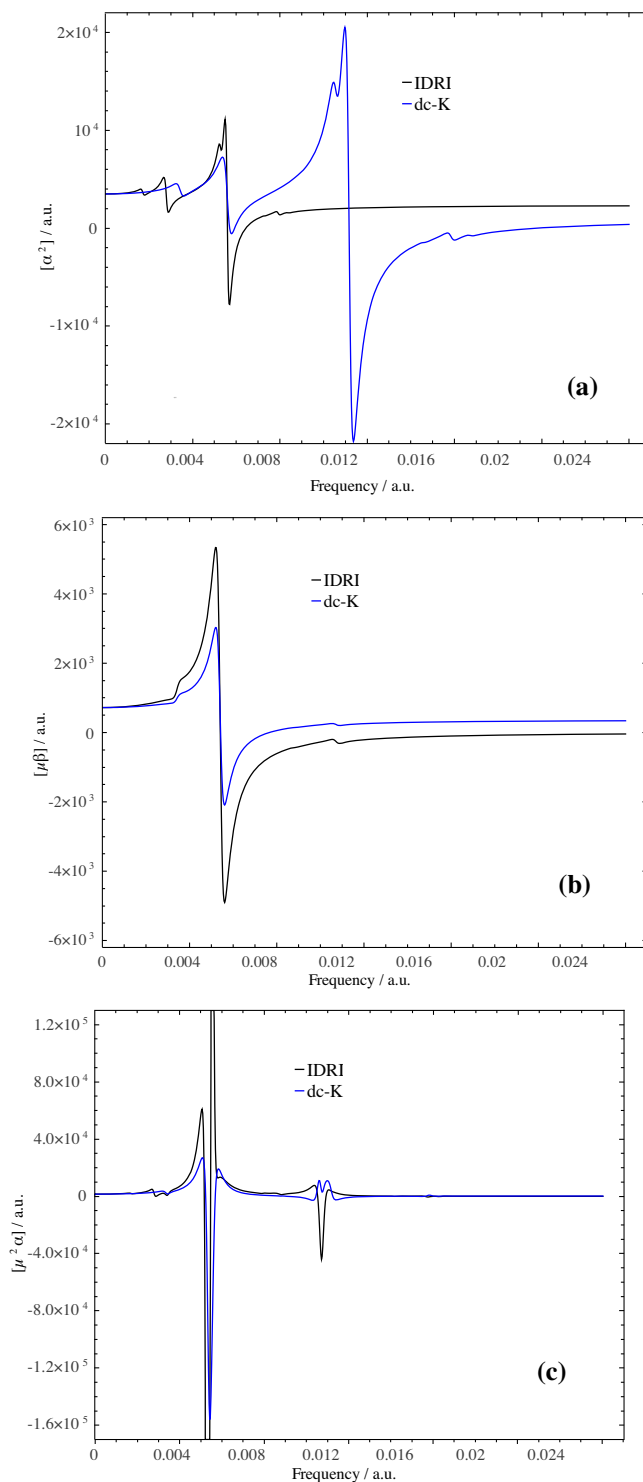


Figure 1. Pure vibrational contributions for the second hyperpolarizability of the ozone molecule: (a) $[\alpha^2]$, (b) $[\mu\beta]$, and (c) $[\mu^2\alpha]$ terms.

lighted. In this case only $(\omega_n - \omega)$ appears. For $[\mu^2\alpha]$ the poles are more severe because products like $(\omega_n - \omega) \times (\omega_n - \omega)$ and $(\omega_n - \omega) \times (\omega_n - 2\omega)$ occur in the denominator.

4. Conclusion

In this work we reported results of vibrational corrections to the first and second hyperpolarizabilities for four triatomic molecules

(O₃, SO₂, N₂O and CO₂) using two approximations: the traditional BKPT approach and a variational scheme (VAR) proposed in a previous work. All calculations of electronic contributions for the properties were carried out through the coupled cluster response theories at the CCSD level. The results obtained through BKPT and VAR methodologies, using the same basis sets of *M*-modes vibrational wave functions, are practically identical for SO₂. For N₂O, there are small differences only for $[\mu\alpha]$ and $[\mu\beta]$. In the case of CO₂, a noticeable difference between BKPT and VAR results is only observed for the term $[\mu^2\alpha]$. This is an understandable result, since this term has a part that appears already in the lowest order in BKPT (first order), which cannot be added without inclusion of anharmonicity in the potential. Larger discrepancies are observed for O₃, for all terms, exception of $[\mu\beta]$. Especially for the term $[\alpha^2]$ there is remarkable difference, which is arising from inclusion of second derivatives of α in the VAR scheme.

The second question address here is the convergence of the variational results as the basis set of harmonic vibrational wave functions is expanded. Our results show that for SO₂ and CO₂ practically converged values are achieved considering the maximum value of the sum of single-mode quantum numbers in the *M*-modes wave functions equal to 3. For SO₂, in especial, the BKPT method up to first general order of perturbation leads to the exact result within our approximation in which only derivatives up to third order in the potential are included. For the terms $[\mu^3]$ and $[\mu^2\alpha]$ of O₃ and N₂O, converged results only are obtained for maximum value of the sum of single-mode quantum numbers equal to 6. In general, the performance of the BKPT method, compared to the variational scheme, is different for the four systems studied here. Strictly speaking, both methods lead to the same results for all terms only for sulfur dioxide. Ozone is the system for which the greatest discrepancies between the two procedures occur.

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