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Perturbed Infrared Spectrum and Vibrational Contribution to Electric Properties of CO₂: An ab Initio SCF Study

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A finite-field method together with analytical computation of field-dependent energy derivatives has been used to compute the vibrational and nuclear relaxation contributions to static electrical properties of carbon dioxide. Comparisons with earlier theoretical results and with experiment are presented, along with an experimental procedure to determine these contributions. These contributions to the static molecular properties are obtained from the infrared spectroscopic modifications (line shifts and changes in line intensities) induced by a uniform electric field.

Introduction

The theoretical study of molecular spectra and molecular electrical properties is becoming an invaluable tool in the identification of chemical compounds. Nowadays, these studies are not only limited to molecules in the gas phase but consider the inclusion of the environment as well. One of the simplest ways to simulate environmental effects is the perturbation of the system by a uniform electric field. Among the various effects on molecular properties related to the presence of a uniform electric field which can be determined theoretically, mainly through ab initio molecular orbital (MO) based methods, one can mention (a) the vibrational Stark effect (VSE) which is reported by the Stark tuning rate, (b) the infrared cross section change, also known as vibrational intensity effect (VIE), and (c) the vibrational and nuclear relaxation contributions to the static polarizability and to higher-order electric properties arising from the change in vibrational wave function upon application of an electric field (α_{vib} and α_{nr} , β_{vib} and β_{nr} , γ_{vib} and γ_{nr} , etc., and in general P_{vib} and P_{nr}).

The aforementioned properties can be systematically studied by means of a number of methods, e.g., derivative Hartree–Fock theory,^{1,2} perturbation theory,^{3–5} or even MO methods using finite-field techniques.⁶ We have recently applied the last approach to study VSE, VIE, P_{vib} , and P_{nr} for a variety of small molecules using both ab initio^{6a–d} and semiempirical^{6e} methods at the SCF level, with good agreement with available experimental data having been found.

The CO₂ molecule has been the subject of increasing interest over time. A particular, highly interesting aspect concerns its spectroscopic behavior upon adsorption in zeolitic cavities, other heterogeneous catalysts, or special cells. For instance, Grodzicki et al.⁷ have reported a normal coordinate analysis of CO₂ in zeolite cavities and compared theoretical results with experimental data. Another study by Shelton⁸ regards the measure of second hyperpolarizability (γ) dispersion of CO₂ using electric-field-induced second-harmonic generation (ESHE). Experimental studies on changes in vibrational frequencies of CO₂ adsorbed in zeolites by Goulay et al.⁹ are especially interesting. Finally, a recent study by Förster and Schumann¹⁰ reports FTIR data for CO₂ adsorbed on ion-exchange A-type zeolites.

The theoretical study of changes in harmonic vibrational spectra and vibrational contributions to molecular properties requires

knowledge of the field-free values. In particular, regarding field-free harmonic vibrational frequencies of CO₂, mention must be made of the study of Yamaguchi et al.¹¹ and Thomas et al.¹² which deal with the basis set and correlation energy influences on equilibrium geometries, dipole moments, harmonic vibrational frequencies, and infrared intensities, showing an absolute average error in harmonic vibrational frequencies with respect to experiment less than 10% at the SCF/TZ2P level. Stanton et al.¹³ have determined harmonic frequencies from analytical MP4 gradients, and Thomas et al.¹² and Besler et al.¹⁴ have performed a similar study for CISD, CCSD, and CCSD(T) levels of theory. Recently, Császár¹⁵ has calculated the anharmonic force field (through sextic order) by means of the MO ab initio techniques. An interesting combined theoretical–experimental study by Ekern et al.¹⁶ on the CO₂...H₃O⁺ complex reports changes in harmonic vibrational frequencies with respect to the CO₂ monomer. In turn, Allen et al.,¹⁷ Maslen et al.,¹⁸ and Martin et al.¹⁹ have recently calculated mechanical and electrical anharmonicity corrections to spectroscopic constants of CO₂. Finally, Morrison and Hay²⁰ have computed vibrationally-averaged polarizabilities, and Gu et al.²¹ have studied vibrational state-dependent polarizabilities of CO₂.

The purpose of the present paper is to analyze static electrical properties of CO₂, which can be separated into electronic, vibrational, and nuclear relaxation contributions using ab initio SCF-MO techniques. To compute these contributions, changes in the harmonic vibrational spectrum of CO₂ when this molecule is placed in a uniform electric field are computed. These theoretical results will increase the basic knowledge of CO₂ and hopefully provide a deeper insight into its spectroscopic and static electrical properties.

In the following section we will outline the methodology used in this study, and in the third section we will present, for various strengths of the applied field, the perturbed infrared spectrum of the CO₂ system, its vibrational Stark tuning rate, and the fractional infrared cross section changes. The results obtained for two orientations of the field and several strengths of the electric field will be analyzed and compared with available experimental data. Furthermore, calculations on the CO₂Li⁺ and CO₂Na⁺ clusters are reported to compare the effects caused by monovalent cations and a uniform electric field on the CO₂ molecule. In the fourth section, we will report the calculated contributions to static molecular electrical properties using the perturbed infrared spectra presented in the third section. Both these contributions and the total values will also be compared with available experimental and theoretical data.

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Methodology

Calculations have been performed at the ab initio SCF level of theory. When the electric field has been included in the one-electron Hamiltonian, a triple- ζ plus polarization (TZ2P)^{22a,b} basis set is used (C and O atoms: [9s5p2d]/(5s3p2d); polarization exponents 0.75 and 0.15 for C and 0.85 and 0.15 for O). Because the TZ2P basis set leads to convergence problems in the SCF processes, the 6-311g(d)^{22c,d} basis set has been used in calculations involving the Li⁺ and Na⁺ cations. Geometries have been reoptimized for each field strength by means of Schlegel's algorithm,²³ whereas harmonic frequencies have been obtained by diagonalization of the mass-weighted matrix of second derivatives of the energy with respect to nuclear displacements. The existence of four null frequencies (three corresponding to translations and one corresponding to rotation about the direction of the applied field) was always checked. Presence of the external electric field has been accounted for by including the electron-field interaction term in the one-electron Hamiltonian. These calculations were performed using the GAUSSIAN 92²⁴ series of programs except for the second-derivative calculations which made use of codes previously developed in our group. This methodology allows to determine easily the position of the energetic minimum and the harmonic vibrational levels for each strength of the applied field, thus permitting the computation of molecular electrical properties by numerical differentiation: the different contributions to electric properties are found^{6d} by fitting the energy values to a power series in the field strength. When the SCF energies of the field-optimized geometries are used, the electronic+nuclear relaxation terms P_{el+nr} (see later) are obtained. Simple subtraction of the purely usual electronic contributions P_{el} , which are obtained without any geometry reoptimization, yields then the nuclear relaxation terms P_{nr} . The vibrational contributions P_{vib} are calculated by fitting the vibrational energies (e.g. the zero-point energies).

Before studying perturbed spectra and molecular electrical properties, we must assess the quality of the calculations performed here. The important point in the present paper is that we are interested more in differences between spectroscopic data rather than in their absolute values. Earlier papers in our group on perturbed infrared spectra have shown SCF calculation yield good results for frequency shifts, line splittings, line intensity changes,^{6a-6c} and also molecular properties contributions.^{6d} Here we have used a fairly large double-polarized basis set because polarization functions are required to describe reasonably well molecular electrical properties.²⁵

We remark that the notation employed in the present paper, which seems rather straightforward to us, can be related to a more traditional notation emerging from perturbation theory, as discussed in a recent paper by Martí and Bishop.²⁶ In particular, for the polarizability α , our terms labeled α_{nr} (nuclear relaxation) and α_{vib} (vibrational) are equivalent to their α_{dis} (change in equilibrium geometry) and α_{curv} (changes in harmonic force constants), which have a more topological meaning.

Vibrational Stark Effect (VSE) and Vibrational Intensity Effect (VIE)

We will present here the vibrational Stark effect (VSE), given by the vibrational Stark tuning rate (δ_{VE}), and the vibrational intensity effect (VIE), given by the fractional infrared cross section change (δ_{SE}), as obtained from perturbed IR spectra of the CO₂ molecule.

Optimization of free-field CO₂ with the TZ2P basis set yields a C–O distance (Table 1) of 1.139 Å, together with the spectroscopic data collected in Table 2. Similarly, with the 6-311g(d) basis set a C–O distance of 1.135 Å is obtained. Harmonic vibrational frequencies and infrared intensities (in parentheses) for the symmetric stretching ν_1 , the doubly degenerated bending ν_2 , and the antisymmetric stretching ν_3 are 1522

TABLE 1: Geometrical Parameters (in angstroms and degrees) and Dipole Moments (in debyes) for the CO₂ Molecule under Different Strengths of an Applied Uniform Electric Field^a

Orientation A			
<i>F</i>	<i>R</i> ₁ (C–O ₁)	<i>R</i> ₂ (C–O ₂)	μ
0.00	1.139	1.139	0.000
0.01	1.147	1.132	0.686
0.02	1.156	1.126	1.374
0.03	1.165	1.120	2.067
0.04	1.175	1.115	2.768

Orientation B			
<i>F</i>	<i>R</i>	θ	μ
0.00	1.139	180.00	0.000
0.01	1.140	178.01	0.360
0.02	1.140	176.01	0.722
0.03	1.140	173.99	1.086
0.04	1.141	171.96	1.456

^a Orientation A stands for the parallel orientation (O₁–C–O₂; the positive sense for electric field applies from O₁ to O₂) of the molecule with respect to the field, and orientation B stands for the perpendicular case. (1 au of electric field = 5.14×10^{11} V/m.)

TABLE 2: Harmonic Vibrational Frequencies (in cm⁻¹) and IR Intensities (in km/mol) for the CO₂ Molecule Submitted to Different Strengths of an Applied Uniform Electric Field^a

Orientation A			
<i>F</i>	ν_1 (<i>I</i> ₁)	ν_2 (<i>I</i> ₂)	ν_3 (<i>I</i> ₃)
0.00	1510 (0.0)	775 (61.4)	2565 (1063.9)
0.01	1506 (6.0)	774 (61.2)	2568 (1053.0)
0.02	1494 (23.3)	773 (60.8)	2571 (1021.0)
0.03	1476 (50.0)	770 (60.0)	2577 (969.9)
0.04	1450 (83.8)	767 (59.0)	2585 (903.1)

Orientation B				
<i>F</i>	ν_1 (<i>I</i> ₁)	ν'_2 (<i>I</i> ' ₂)	ν''_2 (<i>I</i> '' ₂)	ν_3 (<i>I</i> ₃)
0.00	1510 (0.0)	775 (61.4)	775 (61.4)	2565 (1063.9)
0.01	1510 (0.3)	774 (61.4)	775 (61.5)	2564 (1065.0)
0.02	1510 (1.2)	773 (62.0)	775 (61.7)	2559 (1068.3)
0.03	1510 (2.7)	772 (62.7)	775 (62.7)	2552 (1073.9)
0.04	1510 (4.8)	770 (63.7)	775 (63.0)	2541 (1081.9)

^a Orientation A stands for the parallel orientation of the molecule with respect to the field, and orientation B stands for the perpendicular case.

cm⁻¹ (0.0 km/mol), 766 cm⁻¹ (69.3 km/mol), and 2592 cm⁻¹ (1067 km/mol), respectively. Comparison with experimental data ($\nu_1 = 1330$ cm⁻¹, $I_1 = 0.0$ km/mol; $\nu_2 = 667$ cm⁻¹, $I_2 = 1.13$ km/mol; $\nu_3 = 2349$ cm⁻¹, $I_3 = 11.8$ km/mol) shows a fair discrepancy between these results and experiment. This discrepancy has been noted earlier¹⁷ and is quite common to linear triatomic molecules containing multiple bonds. Inclusion of anharmonicity does not improve the results very much.^{17,18} Further, CISD calculations including correlation energy improve them slightly.¹¹ CCSD calculations¹⁴ improve somewhat their quality, as do MBPT calculations.¹³ Simultaneous inclusion of anharmonicity and correlation energy^{18,19} leads to results which are close to experiment. One way to overcome these discrepancies and to bring theoretical results closer to experiment is to scale force constants.²⁸⁻³⁰ However, as mentioned above, the present paper focuses on changes in frequencies rather than on frequencies themselves, so no scaling will be done. We must assert here that our field-free results agree exactly with those reported by Yamaguchi et al.¹¹ Finally, we also want to mention that the methodology used to theoretical determine the vibrational Stark tuning rate (δ_{VE}), and the fractional infrared cross section change (δ_{SE}), has been used previously^{6b,c} and has given good agreement between the experimental and theoretical data.

Because many of our theoretical data are compared with experimental data when the CO₂ molecule is located in zeolite

cavities, a study of the CO₂Li⁺ and CO₂Na⁺ clusters is presented to show that the main effect, in these model systems, has an electrostatic origin. For this purpose, we have analyzed the changes in electrostatic distribution of the free CO₂ molecule produced both by a uniform electric field with an intensity of 0.04 au and by Li⁺ (1.851 Å of O₁) and Na⁺ (at 2.247 Å of O₁) cations placed along the internuclear axis. The changes in charges for O₁, C, and O₂ atoms (obtained from the Mulliken population analyses) generated by the uniform electric field are 0.115, -0.019, and -0.137 au, 0.114, 0.097, and -0.132 for the Li⁺ cation, and 0.093, 0.072, and -0.126 au for the Na⁺ cation, respectively. Thus, these data show the electric field itself causes a charge transfer of 0.137 au from O₁ to O₂, the Li⁺ cation causes a charge transfer of 0.132 au, and the Na⁺ cation causes a charge transfer of 0.126 au. These changes in the electronic distribution of the CO₂ molecule are very similar, showing that the main effect of these monovalent cations is electrostatic.

The changes induced in the electronic distribution either by uniform or by nonuniform electric fields (Li⁺ and Na⁺ cations) create net forces acting on the nuclei; these new forces lead to changes in the whole potential energy surfaces. For instance, the uniform electric field with an intensity of 0.04 au generates net forces on O₁, C, and O₂ atoms of the free CO₂ of 0.053, -0.123, and 0.069 hartrees/bohr, respectively. Likewise, the Li⁺ (at 1.851 Å of O₁) and Na⁺ (at 2.247 Å of O₁) cations generate net forces of 0.048, -0.096, and 0.047 au and 0.037, -0.076, and 0.038 hartrees/bohr, respectively. Then, the effect of the electric field is not only to change the energy but also to modify the location of the stationary points in the potential energy surface, and to change the curvature of this surface. These effects have been already reported in earlier studies.^{6,26}

For the sake of applying the uniform electric field, we must address experimental facts and theoretical clues. Experimental data seem to support two orientations of the CO₂ molecule with respect to the ionic sites in zeolitic cavities. For instance, Förster and Schumann¹⁰ report IR data for both cases; Delaval et al.³¹ report the same in a study of the temperature dependence of the IR spectrum of CO₂. One orientation (A) decreases the symmetry from *D_{∞h}* to *C_{∞h}*, and the other (B) decreases the symmetry to *C_{2v}* when the electric field is applied; both cases have been studied here. Thus, the direction of the applied field has been chosen first by allowing the CO₂ molecule to align itself with respect to the applied field. This leads to parallel orientation A and translates into the condition that there be no imaginary frequencies. The two new non-zero real frequencies correspond to rotations around the two axes perpendicular to the direction of the field. Second, the field has been applied perpendicular to the field-free intermolecular axis, thus causing orientation B. In this case, one pseudorotation has an imaginary frequency that corresponds to a vibration leading to the stable orientation A.

In Table 1 we collect the geometrical parameters for the two orientations of CO₂ when it is influenced by the electric field. For orientation A, which is stable, the C–O₁ bond is lengthened and C–O₂ is shortened. The origin of these modifications can be searched in the changes in the wave function caused by the applied field. Three different changes are induced by the uniform electric field in the molecular orbitals which describe the C–O bonds in the free CO₂ molecule. First, a nodal plane is produced in the 3σ_g and 2σ_u molecular orbitals between C and O₁ atoms. Second, a lowering of the bonding character occurs between C and O₁ atoms of the degenerated 1π_u = 2π_u molecular orbitals. Third, a lowering of the bonding character occurs between C and O₂ atoms of the degenerated 1π_g and 2π_g molecular orbitals. All these changes are due to the increase of the *p* contribution of the carbon atom. In turn, when geometries of the CO₂Li⁺ and CO₂Na⁺ clusters are optimized, the *R*₁ and *R*₂ distances are respectively 1.159 and 1.114 Å for the CO₂Li⁺ species and 1.154 and 1.118 Å for the CO₂Na⁺ cluster. These changes in the C–O

TABLE 3: Stark Tuning Rate ($\delta_{\nu E}$ in cm⁻¹/(V/cm)) and Infrared Cross Section Change (δ_{SE} in cm/V) Values for the Normal Modes of the CO₂ Molecule and Second-Order Stark Tuning Rate (k_1 in cm⁻¹/(V/cm)²) and Second-Order Infrared Cross Section Change (k_2 in (cm/V)²) Values for the Normal Modes of the CO₂ Molecule^a

	Orientation A		
	symm stret	bending	antis stret
$\delta_{\nu E}$	-2.92×10^{-7}	-3.89×10^{-8}	9.53×10^{-8}
k_1	-1.65×10^{-15}	-1.82×10^{-16}	4.33×10^{-16}
δ_{SE}	1.69×10^{-8}	-1.94×10^{-10}	-7.98×10^{-10}
k_2	6.09×10^{-17}	-9.33×10^{-19}	-3.87×10^{-18}

	Orientation B			
	symm stret	bending'	bending''	antis stret
$\delta_{\nu E}$	0.000	-2.33×10^{-8}	0.000	-1.17×10^{-7}
k_1	0.000	-9.83×10^{-17}	0.000	-5.75×10^{-16}
δ_{SE}	1.78×10^{-8}	1.84×10^{-10}	1.38×10^{-10}	8.15×10^{-11}
k_2	6.46×10^{-17}	9.10×10^{-19}	6.53×10^{-19}	3.98×10^{-19}

^a Orientation A stands for the parallel orientation of the molecule with respect to the field, and orientation B stands for the perpendicular case.

bond lengths are very similar to the changes presented in Table 1, showing again that the most important effect in these clusters has an electrostatic origin. The M–O₁ bond lengths are 1.851 and 2.247 Å for Li⁺ and Na⁺, respectively.

For orientation B, which is unstable with respect to rotations, the bond lengths are increased to a much lower extent, and a closure of the OCO bond angle is observed, so linearity disappears. The reason is a breaking of degeneracy of the 1π_u = 2π_u and 1π_g = 2π_g molecular orbitals due to the new *p_z* (*z* is the internuclear axis in the free CO₂) contribution of the oxygen atoms in the π in-plane molecular orbitals, produced by the applied electric field.

Table 2 gathers the values for harmonic vibrational frequencies and infrared intensities, calculated at various strengths of the applied uniform electric field. Finally, we present in Table 3 the Stark tuning rates $\delta_{\nu E}$ (derivative of harmonic frequency with respect to the field strength) and the fractional infrared cross section change δ_{SE} (derivative of the logarithm of the line intensity with respect to the field strength) for each normal mode. To compute $\delta_{\nu E}$ and δ_{SE} , we performed a linear fit to five available points (field strengths of 0.00, 0.01, 0.02, 0.03, and 0.04 au) for each normal mode.

Observation of Table 1 suggests also that the dipole moment is obviously quite influenced by the strength of the applied field. For orientation A, μ increases rapidly up to 2.768 D for a strength of 0.04 au. For orientation B, μ attains only 1.456 D for the same strength. This different behavior is related to the stability of orientation A and to the polarizability of CO₂, which is twice as large for the parallel component than for the perpendicular one.

Regarding harmonic vibrational frequencies (Table 2), our theoretical calculations for orientation A reveal that the bending frequency ν_2 decreases only slightly upon a field strengthening, whereas the symmetric stretching frequency ν_1 decreases substantially; on the contrary, the antisymmetric stretching frequency ν_3 increases only somewhat. Using CO₂M⁺ clusters for the sake of comparison, the changes in the harmonic vibrational frequencies of the CO₂ fragment in the CO₂M⁺ clusters are respectively, for ν_1 , ν_2 , and ν_3 , -5, -24, and 43 cm⁻¹ for Li⁺ and -7, -13, and 25 cm⁻¹ for Na⁺. These values are in agreement with respect to the frequency shifts obtained from an electric field of 0.04 au. For the antisymmetric stretching and the bending of the Na⁺ cluster, the agreement can be considered to be quantitative. On the contrary, for the symmetric stretching, due to the breaking of the symmetric behavior of both oxygen atoms in this normal mode with respect to the free CO₂, the frequency shifts obtained in the clusters are larger than the shifts produced by the uniform electric field. Again, both uniform and nonuniform electric fields induce, in general, similar frequency shifts in the harmonic vibrational

frequencies, because the main effect of the Li^+ and Na^+ cluster is electrostatic. For orientation B, the first effect of the field is to break down the degeneracy of the ν_2 band, due to the lowering of symmetry to C_{2v} : whereas the ν_2'' frequency is not modified, ν_2' shows a slight decrease of the frequency. In turn, ν_1 does not change and ν_3 decreases slightly. Noteworthy pseudorotations (both real for orientation A and one imaginary for orientation B, not reported) appear at very low wavenumbers, corresponding to rotations that are free in the absence of the field, yet become hindered in its presence.

As to line intensities, it is well-known that ν_1 is inactive in the infrared, due to the nonexistent change of the dipole moment upon the occurrence of a symmetric vibration. On the contrary, ν_3 exhibits experimentally a high intensity,^{9,10,31} whereas ν_2 absorbs weakly. Our results show that when in orientation A, the field is strengthened, the ν_2 intensity is almost unchanged, whereas ν_3 decreases its intensity, and ν_1 becomes active. This is the reason why ν_1 is observed for CO_2 perturbed by environmental conditions. For orientation B, the intensities are almost unchanged; the now-active ν_1 band is very weak, and the intensities of ν_2 and ν_3 increase only slightly. In general, thus, the IR spectrum of CO_2 is less perturbed when the field is applied perpendicularly (orientation B), in agreement with experimental data reported by Förster et al.¹⁰ Experimental results of Delaval et al.³¹ for CO_2 in A zeolite also indicate that the intensity of ν_3 does not change very much from the gas phase to the zeolitic cavity, in good agreement with our theoretical calculations.

The interest of the results presented in Table 2 is not only intrinsic and predictive but also interpretative. In the experimental Raman spectrum, ν_1 and $2\nu_2$ are in Fermi resonance, resulting in bands at 1388 and 1285 cm^{-1} , respectively (the so-called ν^+ and ν^- bands). Although early studies attributed ν^+ to ν_1 and ν^- to $2\nu_2$, nowadays this has been reversed and the line showing the largest frequency is attributed mainly to the bending vibration ν_2 . Such a resonance was analyzed some time ago by means of the vibrational self-consistent (VSCF) method by Thomson and Truhlar.³² The results reported in the present work may bring about a further clarification of this assignment. First, our calculations (Table 2) reveal the (harmonic) frequency of $2\nu_2$ to be slightly larger than the (harmonic) frequency of ν_1 , in agreement with experimental data. Table 2 shows that upon application of a field (orientation A) the ν_2 frequency decreases only slightly; on the contrary, the ν_1 frequency decreases noticeably. Experimentally, the changes obtained by Goulay et al.⁹ for the ν^+/ν^- band where the CO_2 is absorbed in CaA zeolite are similar to our theoretical results, whereas physisorption of CO_2 in MgA¹⁰ increases the frequency of ν^+ only slightly and the frequency of ν^- is decreased to a large extent. Similar results for adsorption of CO_2 in CaA zeolite were reported by Grodzicki et al.⁷ Thus, our calculations on ν_1 and ν_2 frequencies are fully consistent with experimental data by Goulay et al.⁹ As to available experimental data on ν_3 and ν_2 vibrations,^{7,9,10} they show an increase in the frequency of ν_3 and a decrease in ν_2 ; these data agree qualitatively with our theoretical results.

From a quantitative point of view, the shifts in this work (Table 2) and the experimental shifts for the bands (ν^- , ν^+ , ν_2 , and ν_3 ; Table 1 in ref 9) are similar (-36 , -7 , -23 , and $+16$ cm^{-1}) except for ν_2 . Variations are obviously reported^{7,10} according to the different environmental conditions at zeolitic cavities. These numbers agree with the line shifts ($\nu_F - \nu_{F=0}$) arising from our theoretical results at the field intensity of 0.03 au for orientation A. Thus, the mean field acting on the CO_2 molecule inside zeolitic trapping sites is predicted to have a strength close to this value. As a matter of fact, for adsorbed CH_4 and CO the field strength was estimated to be close to 0.02 au.^{6a,c}

Our theoretical results for orientation A can be roughly compared to those of the $\text{CO}_2 \cdots \text{H}_3\text{O}^+$ complex studied by Ekern et al.¹⁶ In this study, the $\text{O}-\text{H}_3\text{O}^+$ distance is ca. 2.5 Å; the point

TABLE 4: Parallel and Perpendicular Components of the Total Static Electric Properties (in au) for the CO_2 Molecule and Its Electronic, Nuclear Relaxation, and Vibrational Contributions^a

	elec	vib	nuc rel	rel + vib	total
Parallel					
α_{xx}	22.583	0.153	4.384	4.537	27.120
γ_{zzzz}	503.3	18.9	466.2	485.1	988.4
Perpendicular					
α_{xx}	11.382	0.080	2.771	2.851	14.234
γ_{xxxx}	365.1	28.4	256.0	284.4	649.5

^a Unit equivalences (au to SI units): α , 1 au = $1.648\,78 \times 10^{-41}$ C² m² J⁻¹; γ , 1 au = $6.235\,38 \times 10^{-65}$ C⁴ m⁴ J⁻³.

charge generates a nonuniform electric field, leading ν_3 to increase and ν_2 to decrease, in qualitative agreement with our results; on the contrary, ν_1 increases, although only slightly.

Our results arising from ab initio SCF-MO theory for orientation B can be compared to scarce experimental data. Förster¹⁰ reports a 2- cm^{-1} shift for ν_3 and a -19- cm^{-1} shift for ν_2 . These data do not agree very well with the results gathered in Table 2 for orientation B, where ν_2' decreases slightly its frequency, and where ν_3 decreases it as well as by 24 cm^{-1} for $F = 0.04$ au. The discrepancy here may be explained by the key approximation introduced in the present paper: orientation A, which corresponds to a stable orientation for a uniform electric field, mimics quite well the experimental data for a molecule adsorbed in a zeolite cavity and aligned with the existing field. On the contrary, orientation B (unstable theoretically) does not mimic well the experimental situation when a cation is placed in front of the T-shaped CO_2 molecule; a model including field gradients should be probably considered to study better orientation B. Fortunately, almost all experimental data refer to orientation A, which seems to be the preferred one.

In Table 3, we report the values for $\delta_{\nu E}$ and δ_{SE} for each orientation of the field and each normal mode. The harmonic vibrational frequencies and infrared intensities from the data of Table 2 are obviously consistent with the explanations given in the preceding paragraphs. It is important at this point to remember that $\delta_{\nu E}$ and δ_{SE} values have been obtained with a linear fit to the five available points (ν or $\ln(I/I_0)$ vs F). This gives a simple linear relationship showing the dependence of the IR frequencies and intensities with the electric field, which can be used to compare our results with the available experimental data. However, we should really fit the IR frequencies and the logarithm of the IR intensities for both positive and negative field strengths to be able to evaluate $\delta_{\nu E}$ and δ_{SE} for the field-free case. In this case, $\delta_{\nu E}$ and δ_{SE} would have null values due to the symmetry of the CO_2 molecule for either orientation A or orientation B. Thus, a better approximation to evaluate the dependence of these magnitudes with respect to the electric field strength is given by quadratic expressions, because the third-order terms would also be null due to the same symmetry considerations, i.e., $\Delta\nu = k_1 F^2$, and $\Delta(\ln I) = k_2 F^2$. The values of k_1 and k_2 are given in parentheses in Table 3. It is especially interesting to pay attention to the value of $k_1 = 1/2(\partial^2\nu/\partial F^2)_{F=0.00}$ because, as shown in a previous paper,^{6d} it is directly related to the vibrational contribution of the static dipole polarizability. However, the only experimental data available relate frequencies and intensities with respect to the field to a linear fit instead of to a quadratic one, which will give from experimental data the vibrational contribution to the static dipole polarizability.

Molecular Electrical Properties

In this section we report the electronic, nuclear relaxation and vibrational contributions along with the total values computed for the molecular electrical properties of CO_2 (Table 4). Evaluations of contributions other than electronic require the

molecule to be at a local stationary point of the potential energy surface even when the molecule is perturbed by the field. Because the CO₂ molecule is a nonpolar species, stationary points when the applied field is perpendicular to the intramolecular axis can also be located, and hence both parallel (P_z) and perpendicular (P_x) components of the static electric properties can be computed. Here, the dipole moment (μ) and the first hyperpolarizability (β) have zero values because of the symmetry of the CO₂ molecule, whereas the polarizability (α) and the second hyperpolarizability (γ) have non-zero values.

The values for the electronic component of the polarizability, labeled α_{el} , can be compared to theoretical and experimental data. For instance, Morrison and Hay,²⁰ using correlated wave functions, provided 23.82 and 11.73 au for the values of the parallel α_{zz}^{el} and perpendicular α_{xx}^{el} components of α , respectively. Furthermore, Sekino and Bartlett³³ reported theoretical values of 23.886 and 11.810 au for α_{zz}^{el} and α_{xx}^{el} , respectively. Thus, our results agree fairly well with those results; however, they are still far from the experimental values²⁰ (26.91 and 12.88, respectively), which seems to indicate that contributions other than purely electronic must be considered for polyatomic molecules because there is a 9.8% underestimation of the value predicted by Sekino and Bartlett³³ for the main polarizability with respect to the experimental one.²⁰ In particular, for the noble gases, which have zero values for the nuclear relaxation and vibrational components, the electronic component can be compared directly to experimental data. In a recent paper, Rice et al.³⁴ showed that the electronic component of both dipole polarizability and second hyperpolarizability of the noble gases can be computed with a small error relative to the experimental values at the SCF, MP2, CISD, and CCSD levels using large basis sets.

Our results lead to a mean polarizability α_{el} of 15.082 au, which is very close to the value reported by Laidig and Bader³⁴ in an excellent study of the usefulness of the atoms-in-molecules theory to compute electric properties of molecules through addition of atomic basic components.

For the polarizability α , neither the nuclear relaxation term α_{nr} (which arises from changes in equilibrium geometry caused by the field) nor the vibrational component α_{vib} (changes in zero-point energy) are insignificant. It is especially important to remark that the contribution of the nuclear relaxation term, which shows unusually high values for both parallel and perpendicular components, 4.384 and 2.771 au, respectively, accounts for 19.5% and 16.2% of α . α_{vib} contributions represents less than 1% of the parallel and perpendicular components of α . The sum of these two contributions gives the term of the polarizability which must be added to the electronic contribution to obtain the total value of the CO₂ polarizability. Our results predict the total polarizability tensor to be 27.120 and 14.234 au for parallel and perpendicular components, respectively. From these values, the mean polarizability turns out to be 18.529, which agrees fairly well with the experimental value of 17.56 au.²⁰

As to γ , the most important contributions (Table 4) are due to the purely electronic and to the nuclear relaxation terms. For γ_{zzzz} , the electronic and nuclear relaxation terms account for 50.9% and 47.2%, respectively. For γ_{xxxx} , these two terms account respectively for 56.2% and 39.4%; in this case, the vibrational contribution is more important than for the γ_{zzzz} . This behavior has already been found for other chemical systems, where the nuclear relaxation term can even change the sign of the purely electronic value.⁶⁴

The scarcity of theoretical data on vibrational contributions to electric properties of polyatomic molecules makes it difficult to compare our results with earlier calculations. The only work which deals with these contributions is based on perturbation theory.^{4,5} However, we must be careful in comparing data obtained from our finite-field method with the results arising from a perturbative method. This point is clarified by Martí and

Bishop,²⁶ who establish the relationship between both approaches. For instance, direct comparison can be made between our α_{nr} value and the value of static α'' given by Bishop and Kirtman⁴ because α'' is given by one term which roughly corresponds to α_{nr} . Furthermore, it is not possible to compare the static value of γ'' given by Bishop et al.⁵ because the expression used to calculate γ'' in this last reference does not coincide with our γ_{nr} definition. In a rigorous way, all comparisons must be made between the sum $\gamma'' + \gamma^{ZP}$ (γ^{ZP} stands for zero-point averaged hyperpolarizability) and our $\gamma_{nr} + \gamma_{vib}$.

The values given by Bishop and Kirtman⁴ for the parallel and perpendicular components of α'' are $\alpha''_{xx} = 3.63$ au and $\alpha''_{zz} = 5.11$ au, which agree qualitatively with our results for α_{nr} (Table 4). On the contrary, data obtained from perturbation theory are larger than our α_{nr} values. Another source of data with which to compare is the work of Rinaldi et al.,³⁵ who calculated the nuclear relaxation term (named α_r in their paper) for different molecules by means of the semiempirical MNDO method. These semiempirical results are also of the same order of magnitude as our data ($\alpha_r^{xx} = 4.41$ au and $\alpha_r^{zz} = 3.95$ au); however, they compute the x -component to be higher than the z -component. This is another proof of the sensitivity of these properties to the level of calculation and the basis set size used.

For the second hyperpolarizability γ , comparison of vibrational contributions is only possible with values given by Bishop et al.⁵ ($\gamma_{xxxx}'' = 304.7$ au and $\gamma_{zzzz}'' = 321.0$ au). Our results are in qualitative agreement with perturbation theory data. It is important to note that γ is very sensitive to any change in basis set, and as we mentioned above, we can only compare these results in a qualitative point of view because we are not really comparing the same things.²⁶ As to the electronic component γ_{zzzz}^{el} (503.3 au), its order of magnitude agrees with available experimental data for γ^{el} at zero frequency (1042.3 au) reported by Shelton.⁸ In turn, Sekino and Bartlett³³ provide 700 and 810 au for γ_{xxxx}^{el} and γ_{zzzz}^{el} , respectively. The difference between these values and those calculated in this paper may be due to the differences in basis set sizes. Moreover, their results are obtained at the experimental geometry of CO₂, whereas we have carried out calculations at the geometry optimized with the TZ2P basis set.

Conclusions

The results reported in this study show that the approximation of replacing the complicated field inside real zeolitic cavities by a uniform electric field leads to good agreements with experimental data when the electrostatic interactions are the most important ones. In particular, the results for CO₂ are analyzed and rationalized. The finite-field method for obtaining the different contributions to molecular electrical properties proves to be quite effective and to give reasonable results. Further research concerning inclusion of electron correlation and anharmonicity effects in nuclear relaxation and vibrational contributions to the molecular electrical properties is underway in this laboratory, and the results will be presented in a forthcoming paper.

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