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# Ab initio electro-optical properties crucial to the parity-changing vibrational Raman scattering by gaseous carbon dioxide

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By applying various schemes of the DALTON program suite, the derivatives of the dipole-quadrupole ($\hat{A}$) and dipole-magnetic dipole ($\hat{G}$) polarizabilities by the asymmetric stretching coordinate of $CO_2$ are derived. The $\hat{G}$ derivative was calculated for the first time whereas the obtained cartesian components of $\hat{A}$ favourably agree with the available up-to-date values. Based on the thus derived electro-optical parameters, we provide estimations of the intensity of the forbidden vibrational $\nu_3$ $CO_2$ Raman transition in CO2 which show the leading role of the magnetic elects. The results might be guiding to detect and to quantitatively interpret this novel, vibrational parity-changing Raman process.

**Keywords:** molecular electrooptics, forbidden vibrational Raman spectra of carbon dioxide gas.

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## Introduction

New data on poorly studied electrooptic properties of molecules enable more detailed investigation of molecular structure and may stimulate the development of quantum chemistry methods. Such properties include those governing weak interaction of molecules with the magnetic component of an electromagnetic wave, as well as with the gradient of its electric component. The interaction (E2) of the gradient with the molecular quadrupole induces absorption intensity, which, compared to intensities governed by electric dipole (E1) effects, is described by a small dimensionless ratio $\varkappa_\lambda^2 \equiv (2\pi a/\lambda)^2$, where $a$ is the molecular diameter and $\lambda$ is the light wavelength. Roughly estimated, this ratio for waves in the visible and near-infrared ranges is equal to $10^{-8}-10^{-7}$. Obviously, E2 absorption is greatly suppressed with decreasing frequency, and its detection, especially in the IR range, requires very long light paths. Such absorption was discovered by Herzberg [1] in overtone vibrational transitions in gaseous hydrogen, located in the near-IR range. This discovery was followed by numerous atmospheric and laboratory measurements (e.g, [2–4]) and studies using intracavity spectroscopy (see [5] and references therein).

Magnetic (M1) absorption is characterized by another smallness parameter $\varkappa_m^2 \equiv (v/c)^2$, where $v$ is the orbital electron velocity; detection becomes possible even in the microwave region [6]. In the mid-IR range, vibrational-rotational magnetic transition lines were recently observed [7] within the $\nu_2 + \nu_3$ $CO_2$ absorption band of the Martian atmosphere and identified [8] together with accompanying E2 lines of this band.

For a long time, it was assumed that Raman scattering intensity for optically inactive molecules was entirely due to E1-E1 contributions. Accurate description requires simultaneous consideration of both E2 and M1 interactions, yielding RS amplitudes proportional to $\varkappa_\lambda$ and representing linear combinations of two fully anisotropic mixed-type tensors: the (E1-E2) electric dipole-electric quadrupole polarizability tensor $\hat{A}(\omega)$ and the (E1-M1) electric dipole-magnetic dipole polarizability tensor $\hat{G}(\omega)$. For centrosymmetric molecules, the presence of such tensors leads to anomalous transitions with vibrational parity change, strictly forbidden in the case of E1-E1 polarizabilities.

In chiral molecules, the tensors $\hat{A}(\omega)$ and $\hat{G}(\omega)$ possess isotropic components that play a key role in optical activity and have attracted considerable research interest (see book [9]). For optically inactive molecules, such tensors are fully anisotropic and may manifest in gradient-induced birefringence [10,11] and the linear electro-optic effect on scattered light intensity [12]. The latter effect may occur in all molecules but has not yet been registered, while gradient-induced birefringence exists only in polar molecules like CO, for which the tensors $\hat{A}(\omega)$ [13–16] and $\hat{G}(\omega)$ [14,16,17] were obtained *ab initio*. To compare with existing CO data, we also calculated both tensors, including their dependence on bond length.

So far, experimental data on M1 and E2 contributions to normal RS intensity have been absent, though theoretical aspects of this problem have been studied [18,19]. In [19] RS differential cross-sections were expressed through E1-E2 and E1-M1 polarizabilities, solving the intensity calculation problem.

The subject of this paper is the centrosymmetric linear molecule $CO_2$, for which both E1-E2 and E1-M1 tensors vanish both in equilibrium configuration and at completely symmetric displacements of oxygen atoms; hence, only derivatives with respect to antisymmetric vibrational coordinates are relevant for the vibrational parity change effect. Using a limited basis set, derivatives of $\hat{A}$ for antisymmetric $\nu_2$ and $\nu_3$ modes were first calculated by the self-consistent field method [20,21]. Haskopoulos and Maroulis [22] using MP2 with an extended basis set, obtained significantly more accurate values for the $\hat{A}$ derivative with respect to coordinate $\nu_3$. However, similar data on tensor $\hat{G}$ for $CO_2$ are unavailable, and its calculation is the goal of this work. Using the DALTON software package [23], we also calculated the $\nu_3$-derivative magnitude of polarizability $\hat{A}$.

Based on these data, we determined integrated RS cross-sections for the antisymmetric stretching mode$CO_2$, which may serve as a guide for experimental detection of the new vibrational parity change effect. Note that the algebraic part of calculations is considerably simplified using irreducible spherical tensors (IST) technique [24].

## 1. Theory

### 1.1. Tensor E1-M1

To calculate intensities, molecular and wave characteristics should be separated in the RS transition amplitude expression, after which it takes the form [19]

$$T_{fi}^{E1-M1} = -i\sqrt{2}$$

$$\times \sum_r \left( P_{12}^{(r)}, \sum_k \left[ \frac{\{d_{ki}^{(1)} \otimes m_{fk}^{(1)}\}^{(r)}}{\hbar(\omega_{ki}-\omega_1)} + \frac{\{d_{fk}^{(1)} \otimes m_{ki}^{(1)}\}^{(r)}}{\hbar(\omega_{ki}+\omega_2)} \right] \right)$$

$$- \left( P_{21}^{(r)}, \left[ \frac{\{d_{ki}^{(1)} \otimes m_{fk}^{(1)}\}^{(r)}}{\hbar(\omega_{ki}+\omega_2)} + \frac{\{d_{fk}^{(1)} \otimes m_{ki}^{(1)}\}^{(r)}}{\hbar(\omega_{ki}-\omega_1)} \right] \right), \qquad (1)$$

where $d^{(1)}(=\mathbf{d})$ and $m^{(1)}(=\mathbf{m})$ are the electron dipole and magnetic moments, respectively; ISTs $P_{12}^{(r)} = \{e_1^{(1)} \otimes \{e_2^{*(1)} \otimes n_2^{(1)}\}^{(r)}$ and $P_{21}^{(r)} = \{e_2^{*(1)} \otimes \{e_1^{(1)} \otimes n_1^{(1)}\}^{(r)}$ characterizing electromagnetic field, are constructed on unit vectors describing photon polarization ($e_k^{(1)} = \mathbf{e}_k$) and their wave vectors ($n_k^{(1)} = \mathbf{n}_k$); $\otimes$ denotes convolution of two ISTs into the third one. The four terms on the right-hand side of expression (1) correspond to four Feynman diagrams describing different temporal sequences of instantaneous molecule-field interactions [25]. Thus, the first term corresponds to the situation where photon 1 is absorbed first due to E1 interaction, followed by emission of photon 2 due to M1 coupling. The first term with negative sign results from E1 emission of photon 2 and subsequent absorption of photon 1 due to magnetic M1 interaction. In the non-resonant case considered below, the Placzek approximation applies, and amplitude (1) can be expressed [26] as matrix element $T_{FI}^{E1-M1} = \langle F|T_{el}^{E1-M1}|I\rangle$ of vibrational transition $I \to F$ within the electronic ground state $g = i = f$, where molecular ISTs are obtained by summation over virtual electronic states with fixed nuclear positions. In this case, photon frequencies $\omega_1$ and $\omega_2$ can be replaced by the average frequency $\omega = (\omega_1 + \omega_2)/2$ without loss of accuracy.

Vector components $\mathbf{d}$ appearing in (1), are collinear with electronic momentum $\mathbf{p}$matrix elements; matrix elements of $\mathbf{m}$ and orbital momentum $[\mathbf{p} \times \mathbf{r}]$ are also collinear with each other and, obviously, orthogonal to $\mathbf{p}$ (and consequently, to $\mathbf{d}$). This implies that the scalar term with$r = 0$ in (1) vanishes.

The leading contribution to magnetic amplitude comes from vector term with $r = 1$. Since ISTs of rank 1 built on vectors $\mathbf{d}$ and $\mathbf{m}$are proportional to their vector products [24], we obtain the following expression:

$$T_{el}^{E1-M1}(r=1) = \sum_k \left( \mathbf{P}_{12}, \left\{ \frac{[\mathbf{d}_{kg} \times \mathbf{m}_{gk}]}{\hbar(\omega_{ki}-\omega)} + \frac{[\mathbf{d}_{gk} \times \mathbf{m}_{kg}]}{\hbar(\omega_{ki}+\omega)} \right\} \right)$$

$$- \left( \mathbf{P}_{21}, \left\{ \frac{[\mathbf{d}_{kg} \times \mathbf{m}_{gk}]}{\hbar(\omega_{ki}+\omega)} + \frac{[\mathbf{d}_{gk} \times \mathbf{m}_{kg}]}{\hbar(\omega_{ki}-\omega)} \right\} \right), \qquad (2)$$

where $\mathbf{P}_{12} = -[\mathbf{e}_1 \times [\mathbf{e}_2^* \times \mathbf{n}_2]] = \frac{1}{2}(\mathbf{n}_2(\mathbf{e}_1, \mathbf{e}_2^*) + \mathbf{e}_2^*(\mathbf{e}_1, \mathbf{n}_2))$ $\mathbf{P}_{21} = \frac{1}{2}(\mathbf{n}_1(\mathbf{e}_1, \mathbf{e}_2^*) + \mathbf{e}_1(\mathbf{e}_2^*, \mathbf{n}_1))$. Due to hermiticity of $\mathbf{d}$ and $\mathbf{m}$, we have

$$[\mathbf{d}_{kg} \times \mathbf{m}_{gk}] \equiv [\mathbf{d}_{gk} \times \mathbf{m}_{kg}]^*, \qquad (3)$$

and expression (2) thus becomes

$$T_{el}^{E1-M1}(r=1) = 2\sum_k \left\{ \left( \pi_+, \frac{\omega_{kg}\mathrm{Re}[\mathbf{d}_{kg} \times \mathbf{m}_{gk}]}{\hbar(\omega_{kg}^2 - \omega^2)} \right) \right.$$

$$\left. - i\left( \pi_-, \frac{\omega\mathrm{Im}[\mathbf{d}_{kg} \times \mathbf{m}_{gk}]}{\hbar(\omega_{kg}^2 - \omega^2)} \right) \right\}, \qquad (4)$$

where $\pi_{+-} = \mathbf{P}_{12} \pm \mathbf{P}_{21}$. Magnetic dipole $\mathbf{m}$ contains real operations with electron wave functions and imaginary unit as a common factor, so if $|k\rangle$ is real, $\mathbf{m}|k\rangle$ is imaginary. Further assuming ground state $g$ is singlet, and neglecting spin-orbit interaction, virtual states $k$ in (4) are also singlets but may be $N$-fold degenerate and generally described by complex-valued functions $|k_\alpha\rangle$ $\alpha = 1, 2, \ldots, N$. In this case, contribution from states $k$ is given by projector $P_k = \sum_\alpha |k_\alpha\rangle\langle k_\alpha|$, which remains unchanged under unitary transformation $\hat{U}$ from $|k_\alpha\rangle$ to orthonormal basis of real functions $|k_{\beta'}\rangle$:

$$P_k = \sum_{\alpha\beta'\beta''} |k_{\beta'}\rangle U_{\beta'\alpha} U_{\alpha\beta''}^* \langle k_{\beta''}| = \sum_{\beta'} |k_{\beta'}\rangle\langle k_{\beta'}|. \qquad (5)$$

Consequently, contributions from degenerate virtual states can be related to real wave functions. Similarly, if initial state $g$, is degenerate, analogous unitary transformation can be used that doesn't change expression (4), and averaging over $|g_\alpha\rangle$ set can be replaced with averaging over real functions set $|g_{\alpha'}\rangle$. Considering this, term (4) proportional to $\pi_+$vanishes, and remaining term with $\pi_-$ exactly reproduces the results provided in [19].

### 1.2. Tensor Invariants

***1.2.1. E1-M1-polarizability*** For a linear molecule, arbitrary IST$B^{(r)}$ of rank $r$ in laboratory frame (LF) can be written as

$$B_\sigma^{(r)} = B_r C_\sigma^{(r)}(\Omega), \tag{6}$$

where $C_\sigma^{(r)}(\Omega)$ is a modified spherical harmonic [24], and $B_r$ is a scalar multiplier that can be represented as linear combination (invariant) of Cartesian components of tensor $\hat{B}$, defined in molecular frame (MF). Orienting $Oz$ in MF along molecule axis, we have $B_r = B_0^{(r)}$.

To find amplitude factor $G_1$, $G_0^{(1)}$should be expressed as linear combination of of products of the $\mathbf{d}$ and $\mathbf{m}$ spherical components, then expressed through Cartesian components, noting that due to symmetry only a pair of the cartesian $\hat{G}$ tensor components differs from zero in MF:

$$G_{xy} = -G_{yx} = -2\omega \sum_k \frac{\operatorname{Im}(d_{xkg} m_{ygk})}{\hbar(\omega kg^2 - \omega^2)}. \tag{7}$$

The result shows that $G^{(1)}$ behaves in LF like polar vector of length $G_1 = -\sqrt{2} G_{xy}$. Obviously, selection rules for rotational degrees of freedom and E1-M1 band contour are same as for parallel absorption bands of linear molecules.

Conveniently, reduced E1-M1 tensor $\hat{g} = \hat{G}/\omega$can be introduced, having same dimensionality ($L^4$) as E1-E2 polarizability. When $\omega$ is small compared to electronic frequencies, $\hat{g}(\omega)$ like other electronic polarizabilities exhibits weak positive dispersion.

For completeness, rank $r = 2$IST should also be considered. Omitting electron quantum numbers for brevity, after simple transformations [24] numerator structure on the right-hand side of (1) takes form

$$\{d^{(1)} \otimes m^{(1)}\}_0^{(2)} = \frac{1}{\sqrt{6}}[-(\mathbf{d}, \mathbf{m}) + 3 d_z m_z]. \tag{8}$$

Due to orthogonality of $\mathbf{d}$ and $\mathbf{m}$ and axial symmetry, both terms in square brackets vanish, same as tensor $G^{(2)}$itself.

***1.2.2. E1-E2-polarizability*** Here dipole moment vector convolves with quadrupole moment (IST rank 2), forming either vector ($A^{(1)}$) or IST of rank 3 ($A^{(3)}$). Their invariants are

$$A_1 = -\sqrt{\frac{2}{5}}(A_{z,zz} + 2A_{x,zx}),$$

$$A_3 = \sqrt{\frac{3}{5}}(A_{z,zz} - 4A_{x,zx}/3).$$

Cartesian components of this tensor, known for CO [13,16,17,27] and $CO_2$ [21,22], were also calculated in this work using various DALTON [23] package modifications. While CO exhibits nonzero $A_1$ and $A_3$ at any bond length, their values for $CO_2$ at equilibrium configuration equal zero, so only first derivatives $A_{z,zz}$ and $A_{x,xz}$ with respect to $\nu_3$ coordinate are of interest for us.

## 2. Computational Methods

All calculations in this work used DALTON package [23,28]. Vibrational matrix elements $\hat{A}$ for $CO_2$ for CO2 were obtained in static limit ($\omega = 0$), while $\hat{G}$-tensor was calculated at $\omega = 2.47$ eV $= 0.090771$ a.u. $= 19922$ cm$^{-1}$ since it becomes negligibly small as $\omega$ approaches zero. For CO, we compared our values with Shatz and Kedziora calculations [17] and additionally verified agreement with them at half-reduced frequency. As in work [22], we present data on $CO_2$ both tensors' dependence on antisymmetric displacement $\Delta R = R_1 - R_2$, assuming $Oz$ is directed from atom 2 to atom 1, and $R_1$ and $R_2$ are C-O bond lengths. Obtained dipole-quadrupole tensor components were compared with E1-E2 polarizability characteristics calculated by Chaskopoulos and Maroulis [22]. E1-M1 dipole-magnetic polarizability for CO was then calculated and results compared with published data [16,17]. For the first time, we also present calculated values of $\hat{G}$ derivatives with respect to $\nu_3$-coordinate $CO_2$.

Convergence of tensor $\hat{A}$ matrix elements calculations was studied using augmented correlation-consistent Dunning basis sets both standard (aug-cc-pVXZ) and with core-valence functions [29–31]. Hartree-Fock method was initially used, allowing analytical second-order derivative calculation. For MP2, required polarizability was calculated as finite difference at two field strengths using weak homogeneous field $F = 0.01\ e/a_0^2$. For CCSD polarizability calculations, linear response computational scheme was employed [32]. Calculated properties are expressed as orbital-unrelaxed derivatives of energy (see DALTON l manual, Ch. 33.3 [33]). Polarizability derivatives with respect to $\Delta R$ were computed via finite difference method with step $10^{-2}\ a_0$ using equilibrium C-O bond lengths of 1.1614 Å [34]. Table 1 presents values of static polarizability derivatives $A_{z,zz}$ and $A_{x,zx}$demonstrating high sensitivity to electron correlation. Moreover, these components, especially $A_{x,zx}$exhibit rather slow convergence with increasing basis set. Similar behavior was noted earlier for CO [17]. Notably, adding core-valence functions weakly affected calculation results. Generally, we can state that $\hat{A}$-tensor components found with large basis set agree well with Chaskopoulos and Maroulis calculations [22].

To account for electron correlation influence on dynamic $\hat{G}$-tensor, second-order polarization propagator (SOPPA) method was applied [23]. Convergence testing over extended correlation-consistent basis sets was performed to ensure result accuracy. $Oz$ axis was oriented from C-atom to O-atom. Results for CO molecule obtained in calculations

**Table 1.** Derivatives (in $a_0^3$) of dipole-quadrupole polarizability $CO_2$ with respect to antisymmetric coordinate $\Delta R$

| Method | Basis | $(dA_{z,zz}/\Delta R)_e$ | $(dA_{x,zx}/\Delta R)_e$ |
|---|---|---|---|
| SCF | ADZ | 17.894 | 12.283 |
| | ATZ | 19.292 | 14.367 |
| | AQZ | 19.662 | 15.205 |
| MP2 | ADZ | 21.733 | 13.615 |
| | ATZ (ACTZ) | 23.055 | 15.912 (15.934) |
| | AQZ (ACQZ) | 23.340 | 16.862 (16.938) |
| | A5Z (AC5Z) | | 17.107 (17.103) |
| | A6Z | | 17.198 |
| CCSD | ADZ | 21.233 | 13.572 |
| | ATZ | 22.383 | 15.205 |
| | AQZ | | 16.287 |
| | A5Z | | 16.353 |
| SCF | [7s5p4d2f] | $19.7^a$ | $15.5^a$ |
| MP2 | [7s5p4d2f] | $23.6^a$ | $17.7^a$ |

*Note.* [a] Theoretical values from the work [22].

**Table 2.** $(\mathrm{d}G_{x,y}/\mathrm{d}R)_e$ derivatives of E1-M1 CO polarizability (a.u.) found at two photon energies

| Energy, eV | | 1.24 | 2.47 |
|---|---|---|---|
| Method | Basis | | |
| RHF/Lon[b] | ATZ | −0.694 | −1.599 |
| RHF/Lon[a,b] | ATZ | −0.69 | −1.6 |
| SOPPA/MP2 | ATZ | −0.514 | −1.227 |
| SOPPA/MP2[a] | ATZ | −0.51 | −1.23 |

*Note.* [a] values from the work [17].
[b] gauge-including atomic orbitals (GIAOs) are used [35].

**Table 3.** Derivatives of $(dG_{xy}/d\Delta R)_e$ $CO_2$ ((in a.u.), calculated at photon energy 2.47 eV

| Basis | ADZ | ATZ | AQZ |
|---|---|---|---|
| Method | | | |
| RHF | −1.51 | −1.73 | −1.79 |
| RHF/Lon[a] | −1.56 | −1.75 | −1.80 |
| MP2/SOPPA | −2.44 | −2.65 | −2.68 |
| CCSD/SOPPA | −2.37 | −2.62 | −2.67 |

*Note.* [a] gauge-including atomic orbitals (GIAOs) are used [35].

**Table 4.** Calculated (MP2/SOPPA with AQZ basis) derivatives and vibrational matrix elements (in $a_0^4$) of the mixed polarizability invariants $CO_2$ and their contributions $(I_r)$ to the integrated RS intensity (in $a_0^6$) of the band. $\nu_3$

| $(dg_{x,y}/d\Delta R)_e$ | $(dA_{z,zz}/d\Delta R)_e$ | $dA_{z,zz}/d\Delta R)_e$ |
|---|---|---|
| -18.5 | $23.3;23.6^a;19.7^b;17.0^c$ | $16.9;17.7^a;15.5^b;6.5^c$ |
| $\langle I\|g_1\|F\rangle$ | $\langle I\|A_1\|F\rangle$ | $\langle I\|A_3\|F\rangle$ |
| -2.98 | $-3.87;-4.00^a;-2.04^b$ | $0.07;0.00^a;0.70^b$ |
| $10^6 \times I_1^{E1-M1}$ | $10^6 \times I_1^{E1-E2}$ | $10^6 \times I_3^{E1-E2}$ |
| 1.74 | 0.14 | 0.00 |

*Note.* [a] [22] MP2, [b] [22] SCF, [c] [21] SCF.

(Table 2) fully agree with previously published data by Shatz and Kedziora [17], who used a similar method.

However, first perturbation theory SCF calculation [16] with limited basis gave value $g_{xy} = 8.0\ a_0^4$, approximately two times smaller than SOPPA values and of opposite sign[1]. It should also be noted that static E1-E1 dipole-dipole polarizability values for CO obtained within SCF calculation weakly depend on basis set increase (as seen by comparing [16] and [17,13]results). However, accounting for electron correlation using SOPPA method leads to 10% increase in calculated values, making them very close to Maroulis results [13], obtained via MP4 and CCSD(T) methods. Similar results characterize static E1-E2 polarizability, while for (dynamic) E1-M1 polarizability, electron correlation becomes decisive.

Derivative $g_1$ with respect to $\nu_3$-coordinate $CO_2$ was computed for the first time (Tables 3, 4). Table 4 presents values (in $a_0^4$) of derivatives with respect to $\Delta R$ for both $g_1$ and $A_1$ and $A_3$. Corresponding vibrational transition $0^000 \rightarrow 0^001$matrix elements are also provided, obtained in harmonic approximation by multiplying derivatives with respect to $\Delta R$ by coefficient $\alpha = 0.1516\ a_0$ [36]. Compared to CO SCF case $dA/d\Delta R$ derivatives become more sensitive to basis set dimensionality, remaining approximately 10% smaller than MP2 results of this work (SOPPA, DALTON) and work [22] (GAUSSIAN 98); the latter two are very close to each other.

## 3. Intensity of Raman Scattering with Vibrational Parity Change

For quantitative evaluation of this new effect's intensity, we used expressions from work [19] for $q_2^{-4}\partial\sigma_{FI}/\partial\Omega$ RS cross-sections of E1-E2 and E1-M1 types, calculated per unit solid angle and integrated over frequency. For both contributions, cross-sections are expressed through corresponding vibrational transition matrix element $|I\rangle = |0^000\rangle \rightarrow |0^001\rangle = |F\rangle$:

$$q_2^{-4}\partial\sigma_{FI}/\partial\Omega = q^2 K\Phi_r \langle I|B_r|F\rangle^2, \qquad (9)$$

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[1] Since the direction of the [16] axis is not specified in Amos's study $Oz$, it can be assumed that the discrepancy between the signs of $g_{xy}$ [16] and our work and calculations [17] is caused by the different choice of the axis direction $Oz$. However, all calculations of the E1-E2 [13,16,17], polarizability, which is also sensitive to such a choice, give similar results both in sign and in magnitude, which confirms Maroulis's conclusion [13] about the relatively weak influence of the basis dimension on the value of the E1-E2 tensor CO. Apparently, the discrepancies between $g_{xy}$obtained in [16] and the SOPPA method (this work and [17]), reflect a strong increase in the sensitivity of the results to the value of the basis dimension when going from E1-E2 to E1-M1 polarizability.

where $K$ is a numerical factor ($K^{E1-M1} = 2$, $K^{E1-E2} = 1/6$); $q = (q_1 + q_2)/2 = (\omega_1 + \omega_2)/2c$ denotes average wave vector magnitude, and instead of $B_r$ parameters $g_1 = G_1/\omega, A_1$ or $A_3$ should be used, having dimensionality $L^4$ and weak frequency dependence. An interesting feature of all considered contributions is that total (over secondary photon polarizations) intensity of $90^o$-scattering does not depend on rotating incident radiation polarization by $90^o$ relative to scattering plane, sharply contrasting with properties of usual E1-E1 scattering. Polarization factors values in (9) are as follows [19]: $\Phi_1^{E1-M1} = 1/4$, $\Phi_1^{E1-E2} = 3/20$, $\Phi_3^{E1-E2} = 29/210$. Estimates presented in Table 4 were made for incident light frequency $\omega_1 = 2.47$ eV $= 19922$ cm$^{-1}$, corresponding to effective frequency$\omega = (\omega_1 + \omega_2)/2 = 18747$ cm$^{-1}$connecting $\hat{g}$- and $\hat{G}$-tensor values.

From performed estimates, magnetic channel scattering proves dominant, mainly because its contribution in (9) enters with weight factor $K$ twelve times larger than quadrupole channel. Note also that our $A_1$ amplitude values are very close to [22] results but differ significantly from first SCF calculations [21]. Although similar discrepancy exists for $A_3$ values, all calculations predict very small contribution from rank 3 E1-E2 scattering to $\nu_3$band intensity.

Our estimate of total integral intensity gives $1.9 \cdot 10^{-6}$. This value is comparable to E1-E1 intensity $\approx 10^{-5}$ [37] of weak polarized overtone $2\nu_3$ band, reliably detected in compressed CO2 at $P \gtrsim 5$atm. Therefore, we conclude that discovery and study of $\nu_3$ band in compressed $CO_2$ CO2 Raman scattering spectrum, accompanied by vibrational parity change, is quite feasible with current experimental capabilities.

## 4. Conclusion

Using the DALTON software package, we calculated for the first time the derivative of E1-M1 (dipole-magnetic dipole type) polarizability of $CO_2$ with respect to antisymmetric stretching coordinate. Similarly obtained E1-E2 (dipole-quadrupole) polarizability component derivatives agree well with published data. Accounting for electron correlation using second-order polarization propagator (SOPPA) formalism strongly influences both electrooptic characteristics, especially E1-M1 polarizability. Based on the obtained results, we quantitatively estimated intensity of Raman scattering with vibrational parity change at the excitation of the normal vibrational mode $\nu_2$ in free $CO_2$ molecule. These estimates provide an optimistic forecast for detecting this new effect with current experimental techniques. Similar calculations for antisymmetric mode $\nu_2$ $CO_2$ are planned. Research on vibrational parity change effect will hold similar significance for Raman spectroscopy as magnetic and quadrupole transitions have for one-photon process spectroscopy, and may yield interesting information about molecular electronic dynamics.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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