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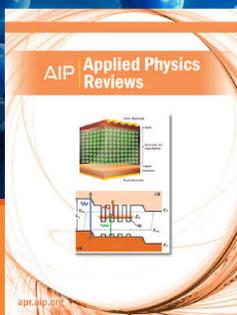
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# Are asymmetric stretch Raman spectra by centrosymmetric molecules depolarized?: The $2\nu_3$ overtone of $\text{CO}_2$

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Molecular vibrations that are not totally symmetrical give rise to depolarized lines [P. Atkins and J. de Paula, *Atkins' Physical Chemistry* (Oxford University Press, UK, 2006), p. 464]. But in the case of stretching vibrations in centrosymmetric molecules, the statement has so far not been conclusively verified. It is the purpose of this article to report a rigorous experimental and theoretical analysis of the  $2\nu_3$  band of  $\text{CO}_2$ —the first overtone of the asymmetrical stretch vibration. The anisotropic spectrum was extracted and its spectral moment calculated from light-scattering measurements, taken at room temperature and for a wide range of  $\text{CO}_2$ -gas densities. Evidence for a near-entirely depolarized Raman band is provided, with integrated depolarization ratio  $\eta_{int} = \frac{6}{7.16}$ , closely approaching the upper bound  $\eta_{max} = \frac{6}{7}$ . Agreement with theoretical predictions is found, on the basis of quality *ab initio* data for polarizability properties, provided that electro-optical and mechanical anharmonicity and intermode coupling effects between symmetric  $\nu_1$  and antisymmetric  $\nu_3$  stretching vibrations are incorporated. © 2011 American Institute of Physics. [doi:10.1063/1.3535599]

## I. INTRODUCTION

In response to a light shining a molecule, electronic clouds are forced to oscillate. If the incident wavelength is not effective enough to allow for resonant excitations of the chemical bonds, only very little energy is lost from the incident light. Of that energy, a part goes to the molecule as excitations of vibrational and rotational states, while another part is scattered away from the molecule as radiation at different directions and wavelengths, and can be recorded as dim light spectra at different frequencies. These are rotovibrational Raman scattering spectra,<sup>1</sup> which help scientists learn much about polarizability tensors  $\hat{\alpha}$  in molecules. Depending on whether it is the mean polarizability  $\bar{\alpha} = \frac{1}{3} \text{Tr}(\hat{\alpha})$  or the anisotropy  $\beta (= \alpha_{\parallel} - \alpha_{\perp}$  for a linear molecule) that governs a scattering process, the spectrum is referred to as isotropic or anisotropic, respectively. Although, generally, the interactions of light on chemical bonds give rise to both those spectra, there exist situations with Raman bands that are totally depolarized. The depolarization ratio of those bands is almost  $\frac{6}{7}$  so they have practically no isotropic spectrum. Such Raman bands lie with Raman transitions in which the vibrational state changes symmetry. An incident beam that is polarized in the direction that is parallel to the scattering plane will merely generate a depolarized spectrum; on the other hand, to see the polarized spectrum, the polarization of the exciting beam must be directed in the perpendicular direction.<sup>2</sup> The corresponding intensities in the two spectra are then referred to as *depolarized* and *polarized*, and denoted  $S_{\parallel}$  and  $S_{\perp}$ , respectively. For an ideal L-shaped experimental setup arrangement, with a zero-aperture scattered-light cone, the two intensities

are related with the anisotropic and isotropic intensity components through the expressions  $S^{\text{ani}} = S_{\parallel}$  and  $S^{\text{iso}} = S_{\perp} - \frac{7}{6}S_{\parallel}$ .

## A. Description

High-resolution Raman experiments in gases have been a matter of long-standing interest. Stoicheff and Weber, and their collaborators, are especially renowned for their pioneering contributions to that field, which has since then been known as “the high-resolution Raman spectroscopy.” Their first experiments to study rotovibrational interactions in gases date back to the second half of 20th century.<sup>3,4</sup> These works soon became the keystone of modern spectroscopy regarding the optical response of various gases and, among such, of carbon dioxide. The first experimental observation of rotovibrational Raman spectra by  $\text{CO}_2$  was reported in the late 1950s for the  $\nu_1 : 2\nu_2^0$  Fermi diad.<sup>3</sup> In the late 1970s, an extensive investigation of the Fermi-doublet of  $\text{CO}_2$  was undertaken, which lasted for nearly a decade.<sup>5</sup> However, in spite of the major advances accomplished since these early studies, comparatively, far too little attention has been focused on the  $2\nu_3$  band of  $\text{CO}_2$ —the asymmetric stretch first overtone. In this respect, the paper by Tejeda *et al.* is so far the only reference to that band.<sup>6</sup> There, only transition moments of  $\bar{\alpha}$  were reported,<sup>6</sup> and with much more emphasis on the  $2\nu_1 : 4\nu_2^0 : \nu_1 + 2\nu_2^0$  triplet and  $\nu_1 : 2\nu_2^0$  diad Fermi resonances of  $\text{CO}_2$  than on the  $2\nu_3$  overtone.

## B. Symmetries

In a general discussion about polyatomic molecules, Atkins and de Paula<sup>7</sup> have stressed that “*only totally symmetrical vibrations give rise to polarized lines in which*

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the incident polarization is largely preserved” and that “vibrations that are not totally symmetrical give rise to depolarized lines.”<sup>8,9</sup> But in centrosymmetric molecules, asymmetric stretch vibrations do not generate Raman spectra. The following question then arises: Is there any recipe for deducing light polarization properties from asymmetric stretch vibrations even though the molecule is centrosymmetric? And if so, is the rule still verified? The answer to both questions is “yes,” and the recipe is “check the first overtone of the vibration.” This is what we show below for the asymmetric stretch  $2\nu_3$  overtone of  $\text{CO}_2$ .

Overtone can indeed be effective tools in circumventing symmetry problems, but in the case of the  $2\nu_3$  overtone of  $\text{CO}_2$  the only existing work has not provided conclusive evidence.<sup>6</sup> The purpose of this paper is to shed light on this issue by making an exhaustive experimental and theoretical analysis of that overtone at room temperature. To this end, the long experience of our group in the area of collision-induced scattering<sup>10,11</sup> was an invaluable guide.<sup>12–16</sup> Almost equally useful in understanding the symmetry concepts treated herein was an analysis, made three decades ago, relative to the problem of the collision-induced mechanisms in Raman scattering for nontotally symmetric vibrations.<sup>17</sup> As for the experiment, the extraordinary sensitivity of our Raman equipment, which has been designed and optimized mainly for the purpose of recording very weak collision-induced spectra (i.e., signals from Raman inactive transitions that can be several hundreds of times weaker than those produced by the  $\text{CO}_2$  overtone<sup>18</sup>) was a guarantee for reliability.<sup>12–16</sup>

Our work revealed that  $2\nu_3$  is a band that is far more anisotropic than isotropic, a result which can also be justified intuitively. Although informal, a hand-waving argument as to the predominance of the anisotropic character of that band is given here, in a few sentences, which can serve as an outline of our rigorous study. According to this argument, the two oxygen atoms,  $\text{O}_a$  and  $\text{O}_b$ , have at any instant two unequal C–O bond lengths, and there are two equivalent, symmetrical arrangements depending on whether it is  $\text{O}_a$  or  $\text{O}_b$  which is closer to carbon. As the three atoms spent most of the time in the vicinity of their turning points (i.e., the positions of a particle’s trajectory at which the velocity arrow instantly switches to the opposite direction), one expects the vibrating  $\text{CO}_2$  to scatter the radiation in a way that is analogous to a pair of C–O bonds that only interact weakly with each other; but interaction-induced light scattering by binary systems is mainly an anisotropic process because, in the dipole-induced dipole approximation, the interaction-induced polarizability of the pair is traceless in the leading order.<sup>10,19</sup> This argument is no longer applicable to totally symmetric vibrations (A1); for more on this subject, see footnote<sup>20</sup> and Refs. 21–23, therein.

A quick estimate of the integrated intensity of the isotropic component of the overtone reveals a value that is some 40 times smaller than the intensity of the anisotropic counterpart. Without entering into further detail on this issue, it is worthwhile noting that this value was found to be in excellent agreement with refined calculations for the isotropic spectrum, but also to match, in order of magnitude, the result reported in the sole prior study of this overtone.<sup>6</sup> This sub-

ject matter is well out of scope here and will be the object of a forthcoming publication both regarding measurements and interpretation.<sup>24</sup>

In Secs. II and III, the anisotropic spectrum is studied, regarding both experimental detection and processing, and its interpretation is made from first principles in terms of zeroth-order spectral moments. To this end, intermode coupling, involving the two stretching vibrations  $\nu_1$  and  $\nu_3$ , and anharmonicity effects (electro-optical and mechanical) had to be incorporated, along with quality *ab initio* data<sup>25,26</sup> for the polarizability anisotropy derivatives.

## II. EXPERIMENTAL

### A. The polarization components

The experiment was conducted with a custom-built side-scattering equipment, along with its extremely sensitive signal detector that was located  $90^\circ$  from the laser’s path. An exhaustive description of this equipment can be found elsewhere.<sup>12</sup> Raman spectral intensities were recorded by room-temperature  $\text{CO}_2$  ( $T = 294.5$  K) for a wide range of gas pressures, which were kept below 55 bars as dictated by the liquefaction properties of  $\text{CO}_2$  at that temperature. Highly purified gas was used, the purity of which was certified by L’Air Liquide company and amounted to 99.998%. The center of the  $2\nu_3$  overtone was seen at  $4673$   $\text{cm}^{-1}$  and the band was recorded over a wide frequency interval, ranging from  $4515$  to  $4810$   $\text{cm}^{-1}$ . In order to ensure measurements as accurate as possible, this interval was separated in four overlapping intervals, respectively centered at  $4560$ ,  $4630$ ,  $4700$ , and  $4770$   $\text{cm}^{-1}$ . Two independent scattering signal components,  $S_{\parallel}$  and  $S_{\perp}$ , were measured as a function of Raman shift  $\nu$ , depending on whether the electric field of the incident beam was polarized in the direction parallel or perpendicular to the scattering plane. The signals were then calibrated and expressed in absolute units ( $\text{cm}^3 \text{ amagat}$ ). Figure 1 illustrates  $S_{\parallel}$  and  $S_{\perp}$  as a function of  $\nu$ . The small dispersion of the points is a measure of the quality of the recorded data. The gas density for

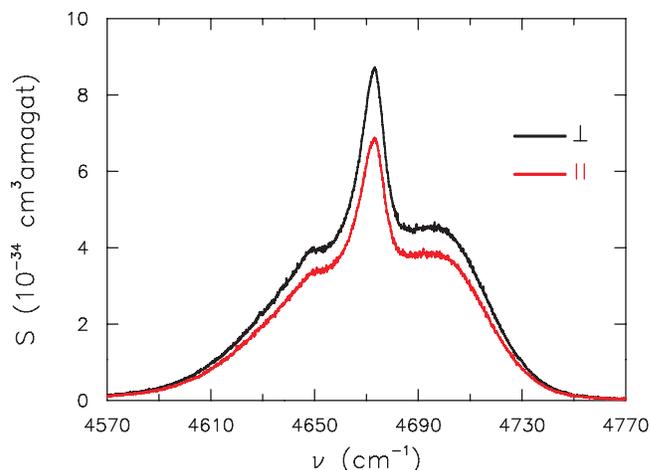


FIG. 1. Absolute spectra  $S_{\perp}$  [black (upper) solid line] and  $S_{\parallel}$  [red (lower) solid line], in units of  $\text{cm}^3 \text{ amagat}$ , recorded in the Stokes side as a function of frequency shift (in  $\text{cm}^{-1}$ ).  $\rho = 55$  amagat.

that experiment was fixed at the upper bound  $\rho = 55$  amagat, which explains why in both spectral components the fine rotational structure has completely collapsed. By contrast with that fine structure, a pronounced structure is seen to persist at the working conditions of temperature and pressure. A quick look down at the figure suffices to identify this structure as the three O, Q, and S branches of the band, depending on whether the selection rule for rotational transitions is  $\Delta J = -2, 0,$  or  $2,$  respectively. This observation is evidence for a huge anisotropic character of the  $2\nu_3$  overtone. Confirmation of this conclusion can be obtained through a different observation, at a glance:  $S_{\parallel}$  and  $S_{\perp}$  are of comparable strengths and shapes overall, which is evidence for a highly depolarized band.

## B. The anisotropic spectrum

The density-dependent anisotropic spectrum  $S^{\text{ani}}$  was deduced from the two recorded components  $S_{\parallel}$  and  $S_{\perp}$ , by means of the expression  $S^{\text{ani}} = 1.010S_{\parallel} - 0.01009S_{\perp}$ . This expression accounts for the finite aperture of the scattered beam, in replacement of the ideal zero-aperture expression  $S^{\text{ani}} = S_{\parallel}$ . Figure 2 shows the profile of the calibrated anisotropic spectrum  $S^{\text{ani}}$ , in units of  $\text{cm}^3$  amagat, as a function of Raman frequency shift (in units of  $\text{cm}^{-1}$ ), for seven values of  $\text{CO}_2$  density, namely, 5, 10, 20, 30, 40, 50, and 55 amagat. At the lowest gas densities  $\rho = 5, 10$  amagat, the otherwise absent rotational structure is now well defined for the branches O and S, whereas still invisible for branch Q. Equally clear is a line-overlapping effect seen to occur with increasing gas density, and which, at 30 amagat, leads to complete coalescence of the rotational lines of O and S branches. To make it sure that the recorded spectrum was indeed due to transitions by single molecules, a rigorous study protocol was established, enabling us to determine the exact way in which

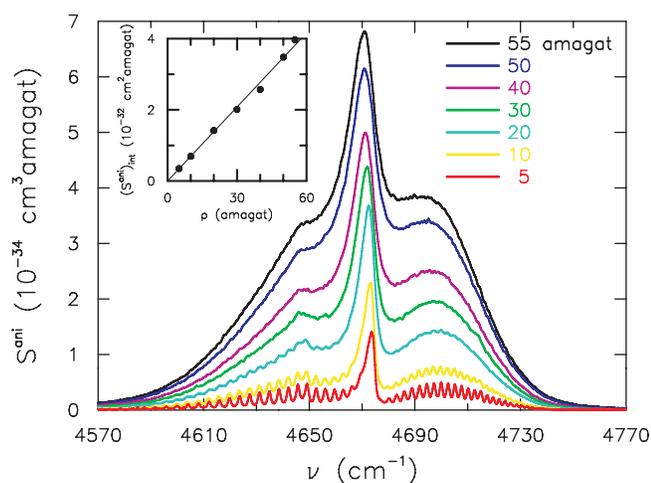


FIG. 2. Absolute anisotropic signal  $S^{\text{ani}}$  in units of  $\text{cm}^3$  amagat as a function of Raman frequency shift (in  $\text{cm}^{-1}$ ). The different curves represent different gas densities: 5, 10, 20, 30, 40, 50, and 55 amagat (in the upward direction). In the inset  $(S^{\text{ani}})_{\text{int}}$  is shown as a function of  $\rho$ ; a behavior that is strictly linear is observed, which is evidence that the recorded band indeed comes from isolated molecules alone, without any appreciable contamination from collision-induced transitions.

the gas density,  $\rho$ , affects the integrated anisotropic signal,  $(S^{\text{ani}})_{\text{int}}$  (see inset in Fig. 2).

Although carbon dioxide exists in 12 stable isotopomeric forms, with a molecular weight ranging from 44 to 49, no isotopic isomer other than the ubiquitous  $^{12}\text{C}^{16}\text{O}_2$  (98.4%) was visible in the figures or could in any way affect our experiment or its interpretation. For all these forms, present at trace levels, either the relative abundances were too feeble to give any visible signature in the spectrum or the position of their bands were outside the domain of interest.<sup>27,28</sup>

## C. The spectral moment

The zeroth-order anisotropic moment was calculated by integrating  $I^{\text{ani}} (= 1.010I_{\parallel} - 0.01009I_{\perp})$ , where  $I_{\parallel} = S_{\parallel}/\rho$  and  $I_{\perp} = S_{\perp}/\rho$ , and then expressed in appropriate  $a_0^6$  units by means of the formula

$$M_0^{\text{ani}} = \frac{15}{2} [2\pi (\nu_0 - \nu_s)]^{-4} \int_{-\infty}^{+\infty} I^{\text{ani}}(\nu) d\nu. \quad (1)$$

In this expression,  $\nu_0$  denotes the laser wavenumber and  $\nu_s$  the wavenumber at the center of the recorded band. We obtain

$$M_0^{\text{ani}}(\text{expt}) = 3.20(15) \times 10^{-3} a_0^6, \quad (2)$$

where the estimated 5% uncertainty was due to systematic errors; “expt” means “experimental.”

From  $S_{\parallel}$  and  $S_{\perp}$ , the depolarization ratio  $\eta = S_{\parallel}/S_{\perp}$  was deduced and found to depend on  $\nu$  only slightly. Aside from the peak of the Q branch, at  $\nu_s (= 4673 \text{ cm}^{-1})$ , which showed just a tiny degree of polarization,  $\eta(\nu_s) = 0.79$ , the values of  $\eta$  remained, all along the frequency interval covered, sensibly equal to the upper limit  $\eta_{\text{max}} (= \frac{6}{7} \approx 0.86)$ . How  $\eta$  depends exactly on  $\nu$  is shown graphically on Fig. 3, which is the most direct means to assess the degree of depolarization of a band and the best way to showcase our findings. Clearly, the  $2\nu_3$  overtone is an almost entirely depolarized band, a result corroborating Atkins’ general assertion.

Rather than a strict rule, Atkins’ assertion is the illustration of the strong propensity of a molecule to undergo a Raman transition that is polarized or depolarized,<sup>9</sup> depending on whether or not the molecule vibrates in a mode that is totally symmetrical. Even so, the disadvantaged spectrum component (anisotropic or isotropic, respectively) cannot be totally absent, so a weak but finite spectrum appears due to that component, which can be detected provided that a high-sensitivity equipment is employed. The fact that none of those

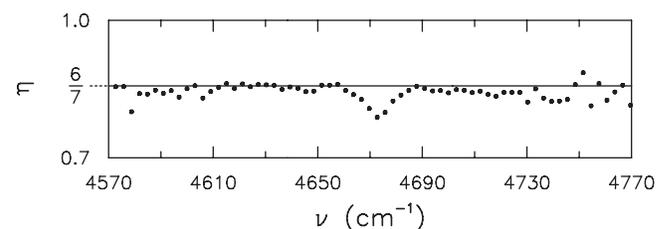


FIG. 3. Depolarization ratio  $\eta$  as a function of Raman frequency shift (in  $\text{cm}^{-1}$ ). Obviously, the overtone is near-fully depolarized.

spectra is strictly absent in a band lies in that, in principle, none of the relevant derivatives of any of the two quantities  $\beta$  or  $\bar{\alpha}$  takes a value that is strictly zero<sup>29</sup> at the equilibrium position.

In order to make this point stand out clearly, an approximate but qualitatively reliable expression for the integrated depolarization ratio [ $\eta_{\text{int}} = (\int_{-\infty}^{\infty} S_{\parallel} d\nu) / (\int_{-\infty}^{\infty} S_{\perp} d\nu)$ ] is given below, along with its simple demonstration. By following the definitions of  $S^{\text{ani}}$  and  $S^{\text{iso}}$  given in the opening section,  $\eta_{\text{int}}$  reads, to zeroth-order approximation for this transition, as

$$\eta_{\text{int}} = \frac{\int_{-\infty}^{\infty} S^{\text{ani}} d\nu}{\int_{-\infty}^{\infty} S^{\text{iso}} d\nu + \frac{7}{6} \int_{-\infty}^{\infty} S^{\text{ani}} d\nu} \approx \frac{\frac{2}{15} (\beta''_{33})_e^2}{(\bar{\alpha}''_{33})_e^2 + \frac{7}{45} (\beta''_{33})_e^2} = 6\chi_{33}^2 (7\chi_{33}^2 + 45)^{-1}, \quad (3)$$

with  $\chi_{33} = (\beta''_{33})_e / (\bar{\alpha}''_{33})_e$ . Here,  $(\beta''_{33})_e$  denotes  $\partial^2 \beta / \partial q_3^2$  calculated at the equilibrium position, and likewise for  $(\bar{\alpha}''_{33})_e$ ;  $q_3$  stands for the normal asymmetric stretching coordinate. Upon use of the *ab initio* data (Ref. 26)  $(\beta''_{33})_e = -0.1346$  a.u. and  $(\bar{\alpha}''_{33})_e = 0.01562$  a.u. for CO<sub>2</sub>, we get  $\eta_{\text{int}} \approx 0.79$ , a value approaching  $\eta(\nu)$  from below (see Fig. 3). Definitely, in spite of its simplicity, this argument is already sufficient to show the strong depolarized character of the  $2\nu_3$  band, in agreement with Atkins' assertion. Obviously, this property arises as a consequence of the exceptionally large value of  $|\chi_{33}|$  for that overtone ( $|\chi_{33}| = 8.6 \gg 1$ ). This conclusion is made all the more interesting by the fact that anharmonicity effects make the value of this parameter be doubled ( $|\chi_{33}| \approx 19$ ).<sup>24</sup> This value of  $|\chi_{33}|$  is uncommonly large, and so too is the case with the value  $\eta_{\text{int}} \approx 0.84$  obtained thereby.

To emphasize the significance of this finding, especially in the general context of linear centrosymmetric molecules, let us now contrast the asymmetric overtone transition of CO<sub>2</sub> with the well-studied problem of the fundamental transition in a homonuclear diatomic molecule. A good example to illustrate this point is the  $\nu_1$  transition of N<sub>2</sub>. According to Atkins' assertion, this transition should generate a band that is strongly polarized, because  $\nu_1$  is a vibration that is totally symmetrical. It turns out that this is indeed the case, as the following short calculation demonstrates. By following a similar argument as the one made above, the following approximate expression is obtained:  $\eta_{\text{int}} \approx 6\chi_1^2 (7\chi_1^2 + 45)^{-1}$ , with  $\chi_1 = (\beta'_1)_e / (\bar{\alpha}'_1)_e$ ;  $(\beta'_1)_e$  stands for  $\partial \beta / \partial q_1$ , and likewise for  $(\bar{\alpha}'_1)_e$ ;  $q_1$  is the normal symmetric stretching coordinate. Upon using the data values for  $(\bar{\alpha}'_1)_e$  and  $(\beta'_1)_e$  reported by Buldakov *et al.*,<sup>30</sup> we obtain  $\chi_1 = 1.2$  and thus  $\eta_{\text{int}} \approx 0.16$ ; with the data of Maroulis,<sup>31</sup> we find  $\chi_1 = 1.1$  and thus  $\eta_{\text{int}} \approx 0.14$ . These values of  $\eta_{\text{int}}$  show that the  $\nu_1$  band of N<sub>2</sub> is polarized to more than 80%. This is in agreement with the statement "only totally symmetrical vibrations give rise to polarized lines in which the incident polarization is largely preserved." For the  $\nu_1$  band of CO<sub>2</sub>,<sup>23</sup> conclusions are similar.

In the remainder of this article, a rigorous zeroth-moment analysis will be made for the  $2\nu_3$  <sup>12</sup>C<sup>16</sup>O<sub>2</sub> overtone toward the successful interpretation of our findings.

### III. THEORETICAL

#### A. Transition matrix element

The polarizability tensor,  $\hat{\alpha}$ , depends on nuclear coordinates and thus on normal coordinates  $q_k, q_l \dots$ . Any of its components,  $\alpha_{\rho\sigma}$ , is a function of the latter coordinates, so it can be expanded into a Taylor series around the equilibrium position "e":<sup>1</sup>

$$\alpha_{\rho\sigma} = (\alpha_{\rho\sigma})_e + \sum_k \left( \frac{\partial \alpha_{\rho\sigma}}{\partial q_k} \right)_e q_k + \frac{1}{2} \sum_{k,l} \left( \frac{\partial^2 \alpha_{\rho\sigma}}{\partial q_k \partial q_l} \right)_e q_k q_l + \dots \quad (4)$$

Upon using this expansion along with perturbation theory, and then retaining components up to the second power in  $q_k q_l \dots$ , the transition matrix element for the anisotropic component of a first overtone reads<sup>32</sup>

$$\langle \nu_l, \nu_j, \nu_i + 2 | \beta | \nu_l, \nu_j, \nu_i \rangle = \frac{1}{2} [(v_i + 1)(v_i + 2)]^{1/2} \left\{ \frac{1}{2} \beta''_{ii} + \beta'_i \frac{k_{iii}}{\omega_i} + \frac{1}{2} \sum_{k \neq i} \left[ \beta'_k k_{iik} \left( \frac{1}{2\omega_i - \omega_k} - \frac{1}{2\omega_i + \omega_k} \right) \right] \right\}. \quad (5)$$

Here,  $\beta = \alpha_{\parallel} - \alpha_{\perp}$  is the anisotropy of  $\hat{\alpha}$ . Symbols  $\nu_i, \nu_j$ , and  $\nu_l$  stand for vibrational quantum numbers of modes  $i, j$ , and  $l$ . Quantities  $\beta'_i (= \partial \beta / \partial q_i)$  and  $\beta''_{ii} (= \partial^2 \beta / \partial q_i^2)$  denote first and second derivatives with respect to normal coordinate  $q_i$ , respectively;  $\omega_i$  is the fundamental frequency of normal vibration  $i$ ;  $k_{iii}$  denotes the cubic force constant of  $i$ ;  $k_{iik}$  couples the vibrations  $i$  and  $k$ . The sum at the rhs of Eq. (5) is over all the fundamental vibrations, yet for the  $2\nu_3$  band of CO<sub>2</sub> the only characteristics of relevance are the normal coordinates  $q_1 (\in \Sigma_g^+)$  and  $q_3 (\in \Sigma_u^+)$ . According to Eq. (5), the overtone transition amplitude depends on the second derivative  $\beta''_{ii}$  (electrooptic anharmonicity) and, because of anharmonic effects, on first derivatives  $\beta'_k$  ( $k \neq i$ ) too. For CO<sub>2</sub>, first derivatives  $\beta'_2$  and  $\beta'_3$  disappear by molecular symmetry and we obtain

$$\langle 00^0 2 | \beta | 00^0 0 \rangle = \frac{1}{\sqrt{2}} \left( \frac{1}{2} \beta''_{33} + \beta'_1 k_{331} \frac{\omega_1}{4\omega_3^2 - \omega_1^2} \right). \quad (6)$$

#### B. The normal coordinates

The symmetric stretch vibration of CO<sub>2</sub> can be described in a way similar to the vibration of a diatomic molecule with bond length  $r = 2R$  and reduced mass  $\mu = m_O/2$ , where  $m_O$  is the atomic mass of oxygen. At the equilibrium separation, the bond length is  $r = r_e (= 2R_e)$ , where  $R_e (= R_{C-O} = 2.192a_0)$  (Ref. 26) is the length of the C–O bond at equilibrium. With these notations,  $q_1 = 2\Delta_1 R \sqrt{\mu \omega_1 / \hbar}$ , where  $\Delta_1 R = R - R_e$ . Using the definition of the rotational constant  $B = \hbar^2 / 2\mu r_e^2$  one obtains  $\Delta_1 R = R_e q_1 \sqrt{2B / \hbar \omega_1}$ . For the asymmetric stretch vibration, the normal coordinate is

TABLE I. Input data needed in Eq. (6). Polarizability derivatives are in atomic units (a.u.); vibrational frequencies and couplings are in  $\text{cm}^{-1}$ .

$\omega_1$	$\omega_3$	$\beta'_1$	$\beta''_{33}$	$k_{331}$
1353.8	2396.5	1.0164 <sup>a</sup>	-0.1346 <sup>b</sup>	-256.3579 <sup>c</sup>

<sup>a</sup>Reference 25.<sup>b</sup>Reference 26.<sup>c</sup>Reference 34.

(Ref. 26)  $\Delta_3 R = R_1 - R_2$ , where  $R_1$  and  $R_2$  denote the elongations of the two C–O bonds. The quantum coordinate  $q_3$  reads (Ref. 33)  $q_3 = (R_1 - R_2)/2b = \Delta_3 R/2b$  where  $b = 0.0401\text{\AA}$ .

### C. The anisotropy derivatives

In the case of the symmetric stretch vibration, coupled-cluster calculations with single, double, and partially triple excitations [CCSD(T)], with carefully designed basis sets done by Maroulis,<sup>25</sup> result in a power expansion for  $\beta$  with a linear term equal to  $\beta(R) - \beta(R_e) \approx 19.35\Delta_1 R$ . Upon using the expression for  $\Delta_1 R$  given above, one gets  $\beta'_1 \approx 1.0164$  a.u. For the asymmetric stretch, the CCSD(T) calculations (Ref. 26) give  $\beta(\Delta_3 R) - \beta(0) \approx -2.93(\Delta_3 R)^2$ , so the required second derivative of the anisotropy reads  $\beta''_{33} \approx -0.1346$  a.u.

Table I gathers all the input data that were needed to calculate the transition matrix-element of Eq. (6). Polarizability derivatives are given in atomic units (a.u.); vibrational frequencies for the two modes and their coupling are in  $\text{cm}^{-1}$ .

### D. The spectral moment

According to Eq. (6) and to Table I, the anisotropic transition matrix-element reads

$$\langle 00^0 2 | \beta | 00^0 0 \rangle = \frac{1}{\sqrt{2}} (-6.7300 \times 10^{-2} - 1.6686 \times 10^{-2}), \quad (7)$$

and thus  $\langle 00^0 2 | \beta | 00^0 0 \rangle = -5.939 \times 10^{-2}$  a.u. Our input data result in a value for the mode coupling [second term of the Eq. (6)] that is of the same sign and order of magnitude as the one for the first term. This coupling brings a correction of 20%, a result stressing the need to go beyond the zero-coupling approximation.

The zeroth-order moment is directly deduced from the matrix-element by means of the expression (Ref. 35)  $M_0^{\text{ani}} = |\langle 00^0 2 | \beta | 00^0 0 \rangle|^2$ . We obtain

$$M_0^{\text{ani}}(\text{th}) = 3.53 \times 10^{-3} a_0^6. \quad (8)$$

It is gratifying to see that this theoretical value (th) is in agreement with the experimental value of Eq. (2) to within 10%.

In reverse, upon assuming  $\langle 00^0 2 | \beta | 00^0 0 \rangle = \pm [M_0^{\text{ani}}(\text{expt})]^{1/2}$  and feeding this value back into Eq. (6), we obtain

$$\beta''_{33} = \begin{cases} 0.193 \text{ a.u.} \\ -0.127 \text{ a.u.} \end{cases} \quad (9)$$

Interestingly, the negative value shown above matches the *ab initio* value of Table I to within 5%; the positive value is a spurious solution. This performance is greater than typical accuracies for second polarizability derivatives, which are often inaccurate by a factor of 2, and lends additional credence to our findings, both regarding the experiment and its interpretation.

## IV. SYNOPSIS

The purpose of this paper was to raise and settle the issue as to the possibility of enlarging Atkins' rule, "only totally symmetrical vibrations give rise to polarized lines in which the incident polarization is largely preserved" ( $\eta \ll \frac{6}{7}$ ); "vibrations that are not totally symmetrical give rise to depolarized lines" ( $\eta \approx \frac{6}{7}$ ), to make it include vibrations that are Raman inactive. The first overtone of the  $\text{CO}_2$  asymmetrical stretch vibration,  $2\nu_3$ , presented itself as the best showcase to illustrate our conclusions. Although  $\nu_3$  is a transition that is inactive in Raman scattering, its first overtone, our study showed, generates a spectrum that is near-entirely depolarized—a result in agreement with Atkins' assertion. Our study is expected to open the door, through the systematic treatment of overtone Raman spectra, to a more systematic look of symmetry concepts in molecules.

<sup>1</sup>D. A. Long, *The Raman Effect. A Unified Treatment of the Theory of Raman Scattering by Molecules* (John Wiley and Sons, Chichester, UK, 2002).<sup>2</sup>In both cases, precautions must be taken to ensure that the emitted radiation is completely unpolarized.<sup>3</sup>B. P. Stoicheff, in *Advances in Spectroscopy*, edited by H. W. Thompson (Wiley, New York, 1959), Vol. 1, pp. 91–174.<sup>4</sup>A. Weber, in *The Raman Effect*, edited by A. Anderson (Marcel Dekker, New York, 1973), Vol. 2, pp. 543–757.<sup>5</sup>H. W. Klöckner, H. Finsterhölzl, K. Srinivasan, H. W. Schrötter, *Appl. Spectrosc.* **32**, 401 (1978); P. Wienecke, H. Finsterhölzl, H. W. Schrötter, and J. Brandmüller, *Appl. Spectrosc.* **40**, 70 (1986).<sup>6</sup>G. Tejada, B. Maté, and S. Montero, *J. Chem. Phys.* **103**, 568 (1995).<sup>7</sup>P. Atkins and J. de Paula, *Atkins' Physical Chemistry*, 8th ed. (Oxford University Press, UK, 2006), p. 464.<sup>8</sup>A totally symmetric vibration is a normal mode with all characters equal to one in the character table. This table is associated with the point group to which the molecule belongs.<sup>9</sup>Strictly, a line is classified as polarized if  $\eta < \frac{6}{7}$ ; if  $\eta = 0$ , the line is fully polarized. A line is classified as depolarized if  $\eta = \frac{6}{7}$ .<sup>10</sup>L. Frommhold, *Adv. Chem. Phys.* **46**, 1 (1981).<sup>11</sup>*Collision- and Interaction-Induced Spectroscopy*, edited by G. C. Tabisz and M. N. Neuman (Kluwer, Dordrecht, 1995).<sup>12</sup>F. Rachet, Y. Le Duff, C. Guillot-Noël, and M. Chrysos, *Phys. Rev. A* **61**, 062501 (2000).<sup>13</sup>F. Rachet, M. Chrysos, C. Guillot-Noël, and Y. Le Duff, *Phys. Rev. Lett.* **84**, 2120 (2000); Y. Le Duff, *Phys. Rev. Lett.* **90**, 193001 (2003); *J. Chem. Phys.* **119**, 1893 (2003); M. Chrysos, A. P. Kouzov, N. I. Egorova, and F. Rachet, *Phys. Rev. Lett.* **100**, 133007 (2008); S. Dixneuf, M. Chrysos, and F. Rachet, *J. Chem. Phys.* **131**, 074304 (2009).<sup>14</sup>I. A. Verzhbitskiy, M. Chrysos, F. Rachet, and A. P. Kouzov, *Phys. Rev. A* **81**, 012702 (2010).<sup>15</sup>M. Chrysos and I. A. Verzhbitskiy, *Phys. Rev. A* **81**, 042705 (2010).<sup>16</sup>I. A. Verzhbitskiy, M. Chrysos, and A. P. Kouzov, *Phys. Rev. A* **82**, 052701 (2010).<sup>17</sup>T. Bancewicz and S. Kielich, *J. Chem. Phys.* **75**, 107 (1981).<sup>18</sup>The signal-at-maximum (in counts per second) generated by the collision-induced simultaneous vibrational transition  $\text{SF}_6(\nu_1) + \text{N}_2(\nu_1)$  was found to be 100 times weaker than the signal of the  $\text{CO}_2$  overtone at its maximum (Refs. 14–16).<sup>19</sup>Y. Le Duff, A. Gharbi, and T. Othman, *Phys. Rev. A* **28**, 2714 (1983).

- <sup>20</sup>For such vibrations,  $O_a$  and  $O_b$  are located symmetrically with respect to carbon, so the bonds of the molecule vibrate as a whole like a breathing sphere (Ref. 21). This is in agreement with the general conclusion drawn by Rudder and Bach that *light scattering for spherically symmetric molecules and atoms should be totally polarized* (their words) (Ref. 22), but also explains why the  $\nu_1$  transition of  $\text{CO}_2$  generates such a very polarized spectrum (Ref. 23); similar arguments apply to the  $\nu_1$  transition of  $\text{N}_2$ .
- <sup>21</sup>Some interesting discussion as to the applicability of the breathing sphere model to  $\nu_1$ ,  $\nu_2$ , or  $\nu_3$  of  $\text{CO}_2$  in solution can be found in G. S. Devendorf, *J. Phys. Chem. A* **104**, 11025 (2000); see also the seminal work by K. S. Schweizer and D. Chandler, *J. Chem. Phys.* **76**, 2296 (1982).
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- <sup>28</sup>In principle, isotope effects can affect observed spectra. The only isotopomeric form of carbon dioxide in a concentration that is large enough to deserve some attention is  $^{13}\text{C}^{16}\text{O}_2$  (1.07%), but the center of the overtone band for this compound is at  $4543.5\text{ cm}^{-1}$ , which is a value lying outside the domain covered in the figures (Ref. 27). The next two isotopomers in order of abundance, namely,  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  (0.4%) and  $^{12}\text{C}^{16}\text{O}^{17}\text{O}$  (0.08%), generate bands that are centered at  $4639.5$  and  $4655.2\text{ cm}^{-1}$ , respectively (Ref. 27). Not only the signatures by these isotopomers were too feeble to be seen in the spectrum, but also their positions were too far away from the center of the recorded band ( $4673\text{ cm}^{-1}$ ) to have an effect.
- <sup>29</sup>In the case of  $2\nu_3$ , only second derivatives with respect to the asymmetric stretching coordinate,  $\partial^2\beta/\partial q_3^2$  and  $\partial^2\bar{\alpha}/\partial q_3^2$ , are relevant. By contrast, in the case of the fundamental  $\nu_1$  transition, the relevant derivatives would be  $\partial\beta/\partial q_1$  and  $\partial\bar{\alpha}/\partial q_1$ .
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