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Collision-induced absorption by CO_2 in the far infrared: Analysis of leading-order moments and interpretation of the experiment

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The diagrammatic theory, developed recently by the authors [Phys. Rev. A **74**, 012732 (2006)], is applied to binary collision-induced properties, with emphasis on induced dipole moments. Assuming rototranslational dynamics to be classical and using irreducible spherical tensor formalism, exact analytical formulas are worked out for the two leading order spectral moments of a collision-induced band by two interacting linear molecules. The formulas are applied to the far infrared absorption by CO_2-CO_2, and permit interpretation of the experiment. This study provides evidence of the adequacy of the electrostatic induction mechanism, provided that hitherto missing vibrational terms of static polarizability are considered.

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I. INTRODUCTION

Collision-induced processes by nonpolar gases are especially relevant to photophysical phenomena, both in Earth's atmosphere and in those of other planets. The interactions between two molecules, *a* and *b*, during an encounter induce variations

$$\Delta\boldsymbol{\mu}_{ab} = \boldsymbol{\mu}_{ab} - (\boldsymbol{\mu}_a + \boldsymbol{\mu}_b) \tag{1}$$

in the pair's dipole moment $\boldsymbol{\mu}_{ab}$, which is now no longer equal to the sum of the dipole moments of the molecules. The same is true also with polarizabilities $\hat{\alpha}_{ab}$. Such variations only last during the brief time-period of the collision, and fade away as soon as the molecules go apart from each other. Collision-induced absorption (CIA) and scattering (CIS) spectra are fingerprints of $\Delta\boldsymbol{\mu}_{ab}$ and $\Delta\hat{\alpha}_{ab}$. Such spectra, though feeble, can sometimes be easily distinguished from ordinary absorption or Raman spectra, because they appear at frequencies at which transitions are forbidden in single molecules [1,2]. The vast areas of intermolecular electro-optics and of fluid microdynamics have much benefited from the rather narrow topic of CIA and CIS, and that is not only true from an academic standpoint. Applied science has also benefited a lot from CIA and CIS, which constantly provide literature with new data on the electro-optical properties of molecules. Those methods are even more appreciable when applied to properties that are hardly accessible by other techniques, providing data as accurate as the ones offered by the most reliable *ab initio* computations. Needless to say, the quality of the multidimensional surface, used to model the anisotropic interaction potential of *a*-*b*, is crucial for collision-induced spectra. When the collision-induced polarization solely stems from long-range interactions, explicit, logical, and predictive systematization of the process is possible by means of Feynman-like diagrams, and of a theory we have recently developed [3] and applied to difficult systems and to delicate situations [4,5].

Collision-induced spectra by carbon dioxide are mainly prints of long-range interactions. This assertion was a key element for a successful interpretation of the ν_3 CIS band of CO_2-CO_2 [6]. A very recent exhaustive analysis of the same band, in the gas mixture CO_2-Ar, validated this assumption [5]. However, when dealing with absorption, past calculations by Gruszka and Borysow showed that CO_2-CO_2 spectra significantly underestimate observation [7,8], thereby raising questions as to the true relevance of short-range effects. Recent calculations by our group showed that sole responsible for those substantial discrepancies, observed in the past between theory and experiment, is the neglect of the vibrational terms of the CO_2 polarizability, and that upon inclusion of these missing terms, agreement with the experiment becomes equally good [4].

In this paper, we deal with CIA by two CO_2 molecules in the far infrared region of the electromagnetic spectrum. Owing to the symmetry of the molecule, the pure rotational spectrum of CO_2 is forbidden in infrared absorption, so the only absorption spectrum in that region is a collisional spectrum. Our purpose is mainly to determine, in light of new elements and data, to what extent the multipole induction model can be trusted, since its adequacy has rather clearly been doubted in the past [7,8]. To this end, we derive and apply exact formulas for the two leading order spectral moments, and we provide an analysis of the CO_2-CO_2 rototranslational problem. Hitherto missing vibrational corrections to the dipole-dipole polarizability of the molecule are introduced, along with a potential energy surface (PES), which properly accounts for the strong CO_2-CO_2 interaction anisotropy. Systematic analysis and critical comparison with observation are made. Throughout the paper, classical mechanics is used, which suffices for the working conditions and system.

II. HISTORICAL BACKGROUND

As mentioned above, the quality of the PES has a major effect on CIA. Effective isotropic PESs are known to be

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unreliable even in systems where interactions are nearly isotropic as is the case in $N_2 \cdots N_2$ [7,9,10]. This is even more true with $CO_2 \cdots CO_2$, notoriously known for its anisotropic interaction. With the advent of high-scale computation techniques, PES modeling has witnessed an impressive progress, which is even more spectacular in the case of $CO_2 \cdots CO_2$ [11,12].

Work on moments of induced spectra using isotropic potentials goes back to the 1970s [13–17]. Anisotropic PESs were first used by Cox and Madden [18], who worked out expressions restricted to the zero-order CIS moment, within the dipole-induced dipole (DID) approximation for $\Delta\hat{\alpha}_{ab}$. Later, Borysow and co-workers [7,9] computed zero-order and second-order CIA moments, and stressed the insufficience of the isotropic approximation in $CO_2 \cdots CO_2$. However, in spite of the significant theoretical advances over the last two decades [7,9,18], there are several good reasons why moment theory should be revised. The formalism of [9] otherwise useful for zero-order and second-order moments cannot be easily extended to allow for moments of a higher order, because it uses the collision frame, which is unsuitable, and the surprisingly complex expressions in which it results [10] are merely a consequence of that use. Although Cox and Madden [18] went beyond the limits set by the collision frame, their derivation is still incomplete, restricted to DID and to the zero-order moment. Since the latest update by Gruszka and Borysow [8], efforts to analytically incorporate the anisotropy of the potential into the CIA properties have seemingly ceased. Ironically, the need for a modern and systematic framework is all the more apparent today, given the urgent need for innovative models relative to carbon dioxide and to its role in the greenhouse effect.

The most appropriate device to overcome the huge complexity of the problem is irreducible spherical tensors (IST) [19], one of the most powerful mathematical tools. Below, exact mathematical expressions are worked out. These expressions, despite the rather specific paper's main goal, are general enough to be also applicable to CIS. To specify the collision-induced property, the more general notation $\Delta X^{(r)}$, of a tensor of rank r, seems preferable, and is henceforward used instead of the familiar $\Delta\boldsymbol{\mu}_{ab}$. As $\Delta\boldsymbol{\mu}_{ab}$ is a vector, CIA is only concerned with $r=1$.

III. IRREDUCIBLE EXPANSIONS OVER SPHERICAL HARMONICS

A. Electro-optical quantities

Collisions only weakly perturb vibrational motion, so vibrational quantum numbers v assigned to single molecules are good quantum numbers. As a result, matrix elements $(\Delta X^{(r)})_{v_f \leftarrow v_i}$, taken between vibrational states $|v_i\rangle$ and $|v_f\rangle$, are key quantities for the calculation of electro-optical properties. These two states, in the particular case of collision-induced rototranslational spectra, coincide with each other and with the ground vibrational state, so transition matrix elements are reduced to expectation values of $\Delta X^{(r)}$. Whatever the situation, the result depends on the orientation of the two molecular axes Ω_a and Ω_b, as well as on the orientation of the intermolecular vector $\mathbf{R}=(R,\Omega)$, the latter assumed to be directed from molecule a to molecule b. In what follows, we confine ourselves to the situation in which external fields only excite vibrations in one molecule, while the other molecule remains in the ground vibrational state. Owing to the indistinguishable nature of a and b, one has to superpose two terms: in the first, the vibrating particle is molecule a while in the second, it is b. Cross terms appearing in the squared matrix element of $\Delta X^{(r)}$ are proportional to $\exp[\pm i(\varphi_a - \varphi_b)]$, with φ_a and φ_b the phases of the vibrational transitions. Those phases are uncorrelated quantities because collisions only slightly perturb vibrational modes, so cross terms are washed out by statistical averaging. Analogous considerations make direct terms to contribute equally. In collision-induced rototranslational spectra, unlike the situation we just mentioned above, initial and final vibrational states coincide, thereby generating interference effects. Below, for pedagogical reasons, we consider a as the receptor and b as the inductor, which is the simplest way to proceed. Upon this assumption, collision-induced intensities by $\Delta\boldsymbol{\mu}_{ab}$ will be nearly twice as high as those generated by $\Delta\boldsymbol{\mu}_a$, the variation of receptor's dipole moment. In order to account for interference, we must of course consider the full property $\Delta\boldsymbol{\mu}_{ab}$, rather than $\Delta\boldsymbol{\mu}_a$ alone. That property, which in the absence of short-range interactions reads $\Delta\boldsymbol{\mu}_{ab}=\Delta\boldsymbol{\mu}_a+\Delta\boldsymbol{\mu}_b$, was automatically considered in our calculations.

According to IST formalism [19], matrix elements $(\Delta X^{(r)})_{v_f \leftarrow v_i}$ can be expressed as an invariant expansion over irreducible ternary products of Racah spherical harmonics:

$$(\Delta X^{(r)})_{v_f \leftarrow v_i} = \sum_{\lambda_a \lambda_b \Lambda \lambda} \mathcal{B}_r(\lambda_a,\lambda_b,\Lambda,\lambda;R)\{\Phi^{(\Lambda)}_{\lambda_a\lambda_b} \otimes C^{(\lambda)}(\Omega)\}^{(r)}. \tag{2}$$

In this expression, $\Phi^{(\Lambda)}_{\lambda_a\lambda_b}$ denotes contraction of two molecular Racah spherical harmonics [20] into an IST of rank Λ [19],

$$\Phi^{(\Lambda)}_{\lambda_a\lambda_b} = \{C^{(\lambda_a)}(\Omega_a) \otimes C^{(\lambda_b)}(\Omega_b)\}^{(\Lambda)}. \tag{3}$$

The aforementioned expansion is subject to the momentum coupling sequences $\vec{\lambda}_a+\vec{\lambda}_b=\vec{\Lambda}$ and $\vec{\Lambda}+\vec{\lambda}=\vec{r}$. Weighting coefficients $\mathcal{B}_r(\lambda_a,\lambda_b,\Lambda,\lambda;R)$ are radial functions. Owing to the central symmetry of the nonvibrating molecules, ranks λ_a and λ_b are even integers. By inversion symmetry restrictions, $(-1)^{\lambda+\lambda_a+\lambda_b}=(-1)^r$, and hence λ is an odd integer. Henceforward, initial and final quantum state labels are dropped for the sake of notational simplicity.

B. Pair distribution function

In classical mechanics, intermolecular potential V for nonvibrating molecules and absolute temperature T is all one needs to fully define a pair distribution function. The latter, normalized over the gas volume, reads

$$G(R,\Omega;\Omega_a,\Omega_b) = \frac{1}{16\pi^2}\exp\left(-\frac{V}{k_B T}\right). \tag{4}$$

As G is a scalar, it can be expanded as follows:

$$G(R,\Omega;\Omega_a,\Omega_b) = \frac{1}{16\pi^2}\sum_{Ll_al_b} G_{Ll_al_b}(R)(\Phi^{(L)}_{l_al_b},C^{(L)}(\Omega)), \quad (5)$$

where $(\Phi^{(L)}_{l_al_b},C^{(L)}(\Omega))$ denotes the scalar product of $\Phi^{(L)}_{l_al_b}$ and $C^{(L)}(\Omega)$. Radial functions $G_{Ll_al_b}(R)$ are obtained by first multiplying both sides of Eq. (5) by $(\Phi^{(L)}_{l_al_b},C^{(L)}(\Omega))^*$ and integrating over Ω_a, Ω_b, and Ω. For two linear rotors, inversion symmetry dictates $(-1)^{L+l_a+l_b}=1$, otherwise $G_{Ll_al_b}=0$. If, in addition, a and b are symmetric molecules, which is the case of CO$_2$-CO$_2$, then ranks l_a and l_b are even integers and so too is L.

IV. SPECTRAL MOMENTS

Spectral moments $M^{(r)}_{2n}$ $(n=0,1,\ldots)$ of an induced property, $\Delta X^{(r)}$, are defined as statistical mean values of the squared time derivatives of that property,

$$M^{(r)}_{2n} = \left\langle\left\langle\left(\frac{d^n\Delta X^{(r)}}{dt^n},\frac{d^n\Delta X^{(r)}}{dt^n}\right)\right\rangle\right\rangle. \quad (6)$$

In this expression, double brackets designate statistical averaging. While in the case of $M^{(r)}_0$ statistical mean values imply that the sole $(\Delta X^{(r)},\Delta X^{(r)})G$ function is integrated and that the integral is taken over coordinate space, in the case of $M^{(r)}_2$ statistical mean values require $(\Delta\dot{X}^{(r)},\Delta\dot{X}^{(r)})G$ to be further multiplied by the velocity Boltzmann density distribution. Needless to specify, in that case integrals must be taken over the complete phase space. Velocity averaging is, in most cases, quite straightforward. Angular integration is done analytically.

A. Zero-order moment

Upon using the definition of zero-order moments, we obtain

$$\begin{aligned} M^{(r)}_0 = \Big\langle \sum & \mathcal{B}_r(\lambda_{1a},\lambda_{1b},\Lambda_1,\lambda_1;R)\mathcal{B}_r(\lambda_{2a},\lambda_{2b},\Lambda_2,\lambda_2;R) \\ & \times(\{\Phi^{(\Lambda_1)}_{\lambda_{1a}\lambda_{1b}}\otimes C^{(\lambda_1)}\}^{(r)},\{\Phi^{(\Lambda_2)}_{\lambda_{2a}\lambda_{2b}}\otimes C^{(\lambda_2)}\}^{(r)}) \\ & \times G_{Ll_al_b}(R)(\Phi^{(L)}_{l_al_b},C^{(L)}(\Omega))\Big\rangle, \end{aligned} \quad (7)$$

where single brackets designate

$$\langle X\rangle = \frac{1}{16\pi^2}\int\int\int XR^2dRd\Omega d\Omega_a d\Omega_b. \quad (8)$$

To further analyze the $M^{(r)}_0$ expression, successive IST recouplings are needed [19]. This allows one to analytically integrate over solid angles, so an analytic expression for $M^{(r)}_0$ is obtained, which reads

$$M^{(r)}_0 = \sum K_r(\lambda_{1a},\lambda_{1b},\Lambda_1;\lambda_1;\lambda_{2a},\lambda_{2b},\Lambda_2;\lambda_2;l_a,l_b,L)I_{Ll_al_b}. \quad (9)$$

In this expression, $I_{Ll_al_b}$ are radial integrals

$$\begin{aligned} I_{Ll_al_b} = 4\pi\int & G_{Ll_al_b}(R)\mathcal{B}_r(\lambda_{1a},\lambda_{1b},\Lambda_1;\lambda_1) \\ & \times\mathcal{B}_r(\lambda_{2a},\lambda_{2b},\Lambda_2;\lambda_2)R^2dR. \end{aligned} \quad (10)$$

They depend on λ_{1a}, λ_{1b}, Λ_1, λ_1, λ_{2a}, λ_{2b}, Λ_2, and λ_2, which, for the sake of notational simplicity, were omitted from Eq. (9). Weighting coefficients K_r are expressed as products of $3nj$-symbols and Clebsch-Gordan coefficients, according to the formula

$$\begin{aligned} & K_r(\lambda_{1a},\lambda_{1b},\Lambda_1;\lambda_1;\lambda_{2a},\lambda_{2b},\Lambda_2;\lambda_2;l_a,l_b,L) \\ & = (-1)^{\lambda_1+\Lambda_2}\Pi_{rr}\frac{\Pi_{\Lambda_1\Lambda_2}}{\Pi_{l_al_b}}\begin{Bmatrix}\lambda_{1a} & \lambda_{1b} & \Lambda_1\\ \lambda_{2a} & \lambda_{2b} & \Lambda_2\\ l_a & l_b & L\end{Bmatrix} \\ & \times\begin{Bmatrix}\Lambda_1 & \lambda_1 & r\\ \lambda_2 & \Lambda_2 & L\end{Bmatrix}C^{L0}_{\lambda_10\lambda_20}C^{l_a0}_{\lambda_{1a}0\lambda_{2a}0}C^{l_b0}_{\lambda_{1b}0\lambda_{2b}0}, \end{aligned} \quad (11)$$

with $C^{\gamma0}_{\alpha0\beta0}$ the Clebsch-Gordan coefficient and $\Pi_{ab\ldots c}=[(2a+1)(2b+1)\ldots(2c+1)]^{1/2}$.

The expression of Eq. (9) is a major result. It extends theory, so that anisotropic interactions between a and b are included, while generalizes the expressions we have previously reported for the less general situation of a collision between a linear molecule and an atom [5]. The isotropic interaction potential approximation, which is the situation most often studied in the literature, is now reduced to nothing but the particular case of $l_b=l_a=L=0$, $\lambda_{1a}=\lambda_{2a}=\lambda_a$, $\lambda_{1b}=\lambda_{2b}=\lambda_b$, $\Lambda_1=\Lambda_2=\Lambda$, and $\lambda_1=\lambda_2=\lambda$. Then, the expression is much simpler mathematically,

$$M^{(r)}_0 = \Pi_{rr}\sum I_{000}(\lambda_a,\lambda_b,\Lambda,\lambda;\lambda_a,\lambda_b,\Lambda,\lambda)\Pi^{-2}_{\lambda_b\lambda_a\lambda}. \quad (12)$$

B. Second-order moment

Second-order moments are more complicated, because kinematical considerations are now involved. The procedure is as follows. The first step consists in taking the first time derivative $\Delta\dot{X}^{(r)}$ at instant zero,

$$\Delta\dot{X}^{(r)}\big|_{t=0} = [(\mathbf{v},\boldsymbol{\nabla}) + (\boldsymbol{\Lambda}_a,\boldsymbol{\nabla}_a) + (\boldsymbol{\Lambda}_b,\boldsymbol{\nabla}_b)]\Delta X^{(r)}. \quad (13)$$

Here, $\mathbf{v}$ is the translational velocity of the pair relative to the center of mass, $\boldsymbol{\Lambda}_a$ and $\boldsymbol{\Lambda}_b$ are the angular velocities $\dot{\Omega}_a$ and $\dot{\Omega}_b$ of the molecules, and $\boldsymbol{\nabla}_a$, $\boldsymbol{\nabla}_b$, and $\boldsymbol{\nabla}$ are gradient operators associated with Ω_a, Ω_b, and $\mathbf{R}$, respectively. The next step consists in squaring the previous expression. Owing to the statistical independence of all three velocities, cross terms appearing in $(\Delta\dot{X}^{(r)},\Delta\dot{X}^{(r)})$ are washed out, so additive partial contributions are assigned to the various degrees of freedom.

1. Translational motion

Relative translation of the molecular pair only involves $(\mathbf{v},\boldsymbol{\nabla})$, thereby resulting in a partial contribution to the second-order moment, which reads

$$M_{2T}^{(r)} = \langle\langle ((\mathbf{v},\boldsymbol{\nabla})\Delta X^{(r)},(\mathbf{v},\boldsymbol{\nabla})\Delta X^{(r)})\rangle\rangle . \tag{14}$$

Here, index "T" denotes translation. To analyze this quantity, algebra is rather lengthy but straightforward, and will be omitted here. Since velocities and positions are uncorrelated, simplifications take place upon statistical averaging, and a simple formula is finally obtained. We content ourselves with the final expression, which is elegant and simple,

$$M_{2T}^{(r)} = \frac{k_B T}{\mathcal{M}} \sum K_r [F(\lambda_1,\lambda_2,L) I_{Ll_a l_b}^{(A)} + I_{Ll_a l_b}^{(R)}]. \tag{15}$$

In this expression, $\mathcal{M}$ stands for the pair's reduced mass, $F(\lambda_1,\lambda_2,L)=[\lambda_1(\lambda_1+1)+\lambda_2(\lambda_2+1)-L(L+1)]/2$ and K_r is given by Eq. (11). This is a remarkable result, which shows contributions to $M_2^{(r)}$ from radial "R" and angular "A" translational degrees of freedom to be independent, whatever the potential and its anisotropy may be. As before, $I_{Ll_a l_b}^{(A)}$ and $I_{Ll_a l_b}^{(R)}$ designate radial integrals. Their expressions are formally identical to that of Eq. (10) for $I_{Ll_a l_b}$, up to the substitution $\mathcal{B}_r \rightarrow \frac{\mathcal{B}_r}{R}$ and $\mathcal{B}_r \rightarrow \frac{d\mathcal{B}_r}{dR}$, respectively. It is easy to verify that in the absence of angular modulation in $\Delta X^{(r)}$, that is for $\lambda_1 = \lambda_2 = 0$, angular contributions vanish. The special case of isotropic potential is treated exactly in the same way as was done above.

2. *Rotational motions*

Here, we outline the derivation of the rotational component of the second-order moment $M_{2R}^{(r)}$ and give final expressions. For details, we address the reader to a subsequent, more technical publication [21]. As mentioned above, $M_{2R}^{(r)}$ is the sum of two individual contributions, $M_{2R}^{(a)(r)}$ and $M_{2R}^{(b)(r)}$, which read

$$M_{2R}^{(k)(r)} = \langle\langle ((\boldsymbol{\Lambda}_k,\boldsymbol{\nabla}_k)\Delta X^{(r)},(\boldsymbol{\Lambda}_k,\boldsymbol{\nabla}_k)\Delta X^{(r)})\rangle\rangle , \tag{16}$$

with $k=a$, b. In order to reach final analytic expressions, Racah harmonics angular gradients must first be calculated. This is possible through the matrix elements of the gradient operator, which are known quantities [19]. Note however that, here, a difficulty arises from the fact that $\{\Lambda_k^{(1)} \otimes \Lambda_k^{(1)}\}^{(g)}$ gives rise to two distinct ISTs with ranks $g=0$ and 2. This situation is met for the first time, as in the somehow analogous translational motion problem only $g=0$ was involved. While the integration of the $g=0$ term over the Boltzmann distribution is straightforward, the case with $g=2$ needs more Racah algebra, because each of the velocities $\boldsymbol{\Lambda}_a$ and $\boldsymbol{\Lambda}_b$ is compelled to be perpendicular to the respective molecular axis. Finally, we obtain

$$M_{2R}^{(r)} = k_B T \sum K_r \left[\frac{I_{Ll_a l_b}}{\mathcal{I}_a} F(\lambda_{a1},\lambda_{a2},l_a) + \frac{I_{Ll_b l_a}}{\mathcal{I}_b} F(\lambda_{b1},\lambda_{b2},l_b) \right], \tag{17}$$

where $\mathcal{I}_k$ is the moment of inertia of molecule k, and K_r are the weighting coefficients met above. In the case of rototranslational CIA by identical molecules, that is, the case we are mainly concerned with here, interchange of the indices of the two molecules has no effect on the radial integrals of Eq. (10) or on the K_1 coefficients, hence each molecule contributes equally to $M_{2R}^{(1)}$.

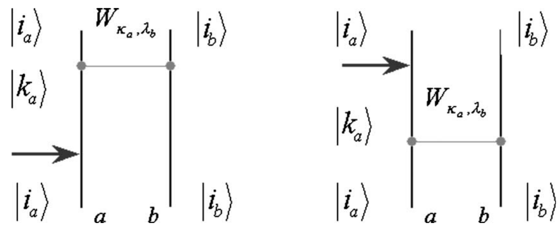

FIG. 1. Feynman graphs depicting the collision-induced polarization in the case when molecule b is the inductor. Time evolves from bottom to top. Intermolecular interaction and absorbed photon are depicted by a horizontal line and by an arrow, respectively. Particular cases discussed in the text are: quadrupole induction $Q_b^{(2)}$ ($\kappa_a=1$, $\lambda_b=2$), hexadecapole induction $Q_b^{(4)}$ ($\kappa_a=1$, $\lambda_b=4$), and induction by the second gradient of the quadrupolar field of molecule b ($\kappa_a=3$, $\lambda_b=2$).

V. ROTOTRANSLATIONAL ABSORPTION BY PURE CO_2

A. Collision-induced dipole moment

Only long-range dipole moment components are here treated, which scale linearly with the total interaction energy W of two nonoverlapping charge distributions. In order to work out analytic expressions, we first express W as a sum of multipole-multipole interactions W_{κ_a,λ_b}, over all possible ranks κ_a and λ_b, and then apply our diagrammatic theory [3]. We assume that the molecule that intercepts the photon, denoted a, is also polarized by the multipolar electric fields generated by b. The situation is illustrated by the two graphs of Fig. 1. In the first graph, radiative coupling precedes intermolecular coupling, while in the second it follows it. In order to account properly for interference effects, two more graphs must be considered (not shown), in which receptor is molecule b. In the calculation, this was done automatically.

According to our theory [3], $\Delta\boldsymbol{\mu}_a$ reads as a sum over the virtual vibronic transitions $0_a \rightarrow k_a$ in molecule a, whereas molecule b remains in the ground state $|0_b\rangle$,

$$\Delta\boldsymbol{\mu}_a = -\sum_{k_a} \left(\frac{\langle k_a|\boldsymbol{\mu}_a|0_a\rangle\langle 0_a 0_b|W|k_a 0_b\rangle}{E_{k_a}-E_{0_a}} + \frac{\langle k_a 0_b|W|0_a 0_b\rangle\langle 0_a|\boldsymbol{\mu}_a|k_a\rangle}{E_{k_a}-E_{0_a}} \right). \tag{18}$$

E_{k_a} and E_{0_a} are the energies of the corresponding states.

Any particular term of W can be written in the form of a scalar contraction [22],

$$W_{\kappa_a,\lambda_b} = (-1)^{\lambda} A_{\kappa_a\lambda_b} \Pi_\lambda \{\{Q_a^{(\kappa_a)} \otimes Q_b^{(\lambda_b)}\}^{(\lambda)} \otimes C^{(\lambda)}(\Omega)\}^{(0)} R^{-\lambda-1}, \tag{19}$$

with $A_{\kappa_a\lambda_b}=(-1)^{\lambda_b}\sqrt{\frac{(2\lambda)!}{(2\kappa_a)!(2\lambda_b)!}}$ and $\lambda=\kappa_a+\lambda_b$. Quantities $Q_a^{(\kappa_a)}$ and $Q_b^{(\lambda_b)}$ denote the 2^{κ_a}-pole and 2^{λ_b}-pole moment tensor operators, with ranks κ_a and λ_b, of molecules a and b, respectively. These operators depend on the electronic and nuclear coordinates of molecules a and b, and so does the resulting multipole-multipole interaction W_{κ_a,λ_b}.

The final expression for the coefficients $\mathcal{B}_1$, introduced in Eq. (2), reads

$$\mathcal{B}_1(\lambda_a,\lambda_b,\Lambda,\lambda;R) = -\frac{1}{\sqrt{3}}\sum_{\kappa_a}(-1)^{\lambda}A_{\kappa_a\lambda_b}\Pi_{\lambda_a\lambda\Lambda} \times \begin{Bmatrix} \lambda_a & \lambda_b & \Lambda \\ \lambda & 1 & \kappa_a \end{Bmatrix} \mathcal{Q}(\lambda_b)\mathcal{P}(\kappa_a,\lambda_a) \times R^{-\lambda-1} - (-1)^{\Lambda}(a \rightleftharpoons b). \tag{20}$$

Note that for linear molecules, any IST can be written as a product of an amplitude factor and a Racah harmonic, which depends on the orientation of the molecule. In the formula of Eq. (20), $\mathcal{Q}(\lambda_b)$ is the amplitude of the $Q_b^{(\lambda_b)}$ tensor operator matrix element, once Racah harmonic $C^{(\lambda_b)}$ has been removed. Quantity $\mathcal{P}(\kappa_a,\lambda_a)$ is likewise the amplitude of the $P_{1\kappa_a}^{(\lambda_a)}$ tensor operator matrix element, upon extraction of its angular dependence. Index λ_a, in $P_{1\kappa_a}^{(\lambda_a)}$, stands for tensor rank; 1 and κ_a indicate that we are only concerned with a dipole-2^{κ_a}-pole polarizability, as a result of the fact that dipole field coupling (2^1) is assumed between the molecule a and the photon. According to standard conventions [23], $\mathcal{Q}(\lambda_k)$ is equal to $Q_{ZZ,\ldots Z}$, a component of the Cartesian multipole tensor in the frame where OZ is the axis of molecule k $(=a,b)$. More algebra is needed to express $\mathcal{P}(\kappa_a,\lambda_a)$ in terms of independent Cartesian components. Useful relations can be found in Ref. [23]. Symbol $(a \rightleftharpoons b)$ in Eq. (20) denotes that the part of the expression preceding this symbol must be considered with interchanged labels. For identical molecules, the interchange makes the $\lambda_a=\lambda_b$ even-Λ terms vanish. Note that in all cases, indices are subject to momenta addition rules $\vec{\lambda}_a+\vec{\lambda}_b=\vec{\Lambda}$, $\vec{\Lambda}+\vec{\lambda}=\vec{1}$, $\vec{1}+\vec{\kappa}_a=\vec{\lambda}_a$, and $\vec{1}+\vec{\kappa}_b=\vec{\lambda}_b$. For given λ_a and λ_b, the first two of these rules put restrictions on the allowed values of Λ.

1. Multipolar induction mechanisms

Quadrupole induction ("Q2") scales with intermolecular separation as R^{-4}, and is by far the dominant mechanism. Hexadecapole induction ("Q4") falls off like R^{-6}, so one may expect it also to have some non negligible effect on the spectrum; at least, that is one of the conclusions Gruszka and Borysow arrived at [7], who found that hexadecapole induction has an impact of about 10% on the integrated intensity.

Along with Q4, induction by the second gradient of inductor's quadrupolar field is also a mechanism that scales as R^{-6}. Such a mechanism has never been considered in CO_2 before this paper, but it should not be neglected if Q4 is to be taken into account. Upon consideration of this mechanism, tensor $\hat{E}$, referred to as the dipole-octupole polarizability, enters the play. This opens up two possibilities. In the first, $(\lambda_a,\lambda_b)=(2,2)$. However, as $\lambda=5$, only $\Lambda=4$ is allowed, hence $\mathcal{B}_1$, which is proportional to $\mathcal{P}(3,2)$, is cancelled out by $a \rightleftharpoons b$ interchange. This shows that the second-rank IST component of $\hat{E}$ has no contribution to the process. This is not the case with the second possibility: the fourth-rank IST component. The latter, being proportional to $\mathcal{P}(3,4)$, is compatible both with $(\lambda_a,\lambda_b)=(4,2)$ and with (2,4), owing to the interchanging role of receptor and inductor. For both (λ_a,λ_b), all three values $\Lambda=4,5,6$ are allowed and contribute. We obtain $\mathcal{P}(3,4)=\frac{2}{\sqrt{7}}(E_{Z,ZZZ}+2E_{X,XXX})$, in agreement with past studies [24]; in this expression, $E_{X,XXX}$ and $E_{Z,ZZZ}$ are Cartesian components of $\hat{E}$ in the molecule-fixed frame.

Note that Eq. (18) is not restricted to some particular multipole-multipole interaction. Moreover, unlike all previous approaches in which Cartesian tensors were used, algebra here is much simpler.

2. Dispersion forces

The next order term in the asymptotic expansion of $\Delta\boldsymbol{\mu}_a$ arises from dispersion interactions, which fall off as R^{-7} [24,25]. They produce two distinct effects, which can be viewed as two different polarization mechanisms. The first is back induction, a feedback response of the molecule that can be understood and studied with classical mechanics. The other, a mechanism with no classical analog, lies with the virtual vibronic excitations that simultaneously occur in the two molecules. Unlike the former mechanism, which is easily understood in terms of conventional static polarizabilities, the latter one requires data on dipole-dipole-quadrupole polarizability at an imaginary frequency, $B(i\omega)$ [24,25]. No such data are available for CO_2, but works in nitrogen have shown this particular mechanism to be roughly as significant as back induction [25]. Thus, moment calculations consisting in retaining back induction effects while disregarding simultaneous virtual vibronic excitations lose much of their meaning. According to Bohr and Hunt [25], these two mechanisms are expected to produce opposite effects of comparable significance. They will be neglected both together.

In the remainder of the paper, we confine ourselves to those induction mechanisms that fall off not faster than R^{-6}. The forthcoming subsection helps reader figure out how much, according to our calculations, each of the retained mechanisms truly contributes. All effects will be calculated with updated data and with appropriate inclusion of other, hitherto missing corrections.

B. Comparison between theory and experiment

1. Quadrupole induction mechanism

Table I shows CO_2 input parameters. The entries of the first row are *ab initio* values for the dipole-dipole, $\hat{\alpha}$, and the dipole-octupole, $\hat{E}$, polarizability tensors, as well as for the quadrupole, $\mathcal{Q}(2)$, and hexadecapole, $\mathcal{Q}(4)$, moments [26]. Values for $\hat{\alpha}$ and $\hat{E}$ account only for electronic contributions. The value $\mathcal{Q}(2)=-3.19$ a.u. is 5% greater than the one used by Gruszka and Borysow [7], who have found long-range induction to underestimate observation by some 30%. Now, with the improved $\mathcal{Q}(2)$ input, discrepancies are getting even larger by some extra 10%, but they are again reduced by about the same amount upon use of the updated PES input [11,12] in comparison with earlier site-site PESs.

2. Hexadecapole and second-gradient induction mechanisms

The next step is to add hexadecapole interactions, and to complement them with second-gradient induction. Unlike

TABLE I. Input data (in atomic units) for spectral moment calculations.

Contribution	α_{ZZ}	α_{XX}	$\mathcal{Q}(2)$	$\mathcal{Q}(4)$	$E_{Z,ZZZ}$	$E_{X,XXX}$
Electronic	27.1[a]	13.0[a]	−3.19[a]	−1.6[a]	187.6[b]	−68.9[b]
Vibrational	2.98	1.67	0	0	−5.0	
Total	30.1	14.7	−3.19	−1.6	182.6	−68.9

[a] CCSD(T) [26].

[b] Second-order Møller-Plesset [26].

$\mathcal{Q}(2)$, whose improvement (along with improvement in the PES) was not strong enough to allow for significant changes in the spectrum, in the case of $\mathcal{Q}(4)$ recent coupled cluster with single, double, and partial triple excitations [CCSD(T)] computations [26] result in a value that is dramatically different from the value −10.8 a.u. used in [7]. In light of the updated data for both $\mathcal{Q}(4)$ and PES, Q4 now appears to play only a minor role in the spectrum (−1.5%), a conclusion in conflict with previous claims [7] that Q4 would be responsible for −10%. Moreover, according to our calculations, the inclusion of the hitherto missing second-gradient induction almost completely cancels out the small effect of the hexadecapole interaction. In other words, after inclusion of all these induction mechanisms that go like R^{-6}, there is still no perceptible improvement in the spectrum, in comparison with the effect of Q2 alone.

3. Vibrational polarizabilities

Contrary to the corrections we extensively discussed above, vibrational corrections to the static polarizability, $\hat{\alpha}$, play a decisive role in searching for agreement between theory and experiment. No such corrections have ever been considered before. Their contribution is extremely pronounced because vibrational frequencies of CO_2 are substantially higher than the typical frequency range of the rototranslational band. How to include these terms, in the case of $\hat{\alpha}$, is a rather easy task because reliable measurements of vibrational dipole oscillator strengths are available [27]. As shown in Table I, vibrational corrections to $\hat{\alpha}$ are responsible for more than 12% of the polarizability.

The effect of the vibrational polarizabilities on the spectral moments is shown in Table II. This table allows for comparison between the full moment values, $M_{2n}^{(1)}$ $(n=0,1)$, and the values $M_{2n,el}^{(1)}$ obtained within the electronic polarizability approximation $\hat{\alpha} \approx \hat{\alpha}_{el}$. Owing to the minor role of the second-gradient induction mechanism, no vibrational corrections to tensor $\hat{E}$ were needed.

PES anisotropy has a strong effect on moments. In order to quantify this effect, moments are first computed within the effective isotropic potential approximation. In this case, only I_{000} radial integrals appear, resulting in values $M_{2n,iso}^{(1)}$ that exceed both the observation and the exact theoretical results. The observed heavy mixing between the various terms of the induced polarization is a well-expectable result, owing to the very anisotropic character of the CO_2-CO_2 pair. These interferences turned out to produce a negative overall effect on the spectrum. Upon inclusion of vibrational corrections, zero-order moments $M_0^{(1)}$ are increased by 25%. An additional 10% comes from the updated PES input, so theory now successfully matches the experiment. Second-order moments $M_2^{(1)}$ are affected in exactly the same way as $M_0^{(1)}$. The best results (underlined entries) are obtained when all corrections have been taken into account. Reduced second moments, $\bar{M}_2^{(1)}=M_2^{(1)}/M_0^{(1)}$, are rather insensitive to the PES model, and are only little affected by its anisotropy. This would no longer be true, upon altering the long-range character of $\Delta\boldsymbol{\mu}_a$ or its dependence on the rotational degrees of freedom. Square roots of reduced second moments, $(2\pi c)^{-1}\sqrt{M_2^{(1)}/M_0^{(1)}}$, are also quantities of major physical importance as a means to assess the extent of a spectral band. For Gauss profiles, these quantities provide the band's halfwidth $\Gamma/2$ (cm^{-1}) at $1/\sqrt{e}$ maximum.

TABLE II. Zero-order and second-order spectral moments calculated at $T=298$ K, with and without vibrational corrections to the static polarizability, $M_{2n}^{(1)}$ and $M_{2n,el}^{(1)}$ $(n=0,1)$, respectively. $M_{2n,iso}^{(1)}$ denote moments within the isotropic potential approximation. Zero-order moments are expressed in $e^2a_0^5$ units; second-order moments are in $e^2a_0^5$ cm^{-2}. Best results are marked by underlined entries. Experimental values (expt.) are shown for comparison.

PES	$M_0^{(1)}$	$M_{0,el}^{(1)}$	$M_{0,iso}^{(1)}$	$M_2^{(1)}\times 10^{-4}$	$M_{2,el}^{(1)}\times 10^{-4}$	$M_{2,iso}^{(1)}\times 10^{-4}$
[29]	7.25	5.78	11.2	1.29	1.03	1.82
[28]	7.22	5.75	12.2	1.35	1.08	2.01
[12]	8.03	6.40	10.8	1.33	1.06	1.74
[11]	$\underline{8.32}$	6.64	12.3	$\underline{1.44}$	1.15	2.00
expt. [30]	10 ± 2			1.5 ± 0.2		

When focusing on the way in which intensity is shared between the various degrees of freedom, we find that the contribution of molecular rotation to $M_2^{(1)}$ is twice as large as the contribution of translation, and that it is shared equally between the two molecules. Specifically, the three independent motions, i.e., molecular rotation $M_{2R}^{(1)}$, angular translation $M_{2T}^{(1)(A)}$ and radial translation $M_{2T}^{(1)(R)}$, scale, according to our calculations, as 69.9:13.3:16.8. This result is in excellent agreement with the ratio $M_{2R}^{(1)}:(M_{2T}^{(1)(A)}+M_{2T}^{(1)(R)})=70:30$, obtained by Ho, Birnbaum and Rosenberg with an isotropic PES [30].

As an overall remark, the larger the molecule the milder the spectral manifestations of short-range polarization terms in comparison to long-range ones. This is a general trend, which stems from considerations related both to the value of intermolecular separation at which the steep barrier of the intermolecular potential energy occurs and to the typical magnitude of the electrostatic induction around that separation. While, strictly, short-range polarization terms are not absent in CO_2-CO_2, their effect on the collisional spectrum is hindered by collisional statistics since electron exchange and orbital overlap become effective only at separations close to the unified-molecule limit. Our calculations and their comparison with available data from laboratory CIA experiments in carbon dioxide have shown this to be the case for low, ambient, and moderately high temperatures. Only at very high temperature can short-range CO_2-CO_2 effects be seen with CIA spectroscopy.

VI. SYNOPSIS

Our diagrammatic theory was applied, along with irreducible tensor formalism, to the room-temperature rototranslational absorption band of pure CO_2, which is forbidden in ordinary absorption. We interpreted the CO_2-CO_2 experiment and we analyzed the principal characteristics of the spectrum in terms of rotational and translational motions of the interacting molecules. We provided evidence of the adequacy of long-range polarization terms between CO_2 molecules, a result that rules out the role of short-range polarization terms. The role of the hitherto missing vibrational dipole-dipole polarizability corrections proved to be crucial for agreement between theory and experiment. In the case of N_2, whose CIA spectrum has long and successfully been interpreted on the sole basis of the electrostatic induction model, no such corrections exist. This may explain why the matter was never raised before our work. Our analysis opens up new perspectives for understanding and interpretation of spectra by nonpolar gases that are ubiquitous in atmospheric environments.

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