

Fermi resonance in CO₂: Mode assignment and quantum nuclear effects from first principles molecular dynamics

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Vibrational spectroscopy is a fundamental tool to investigate local atomic arrangements and the effect of the environment, provided that the spectral features can be correctly assigned. This can be challenging in experiments and simulations when double peaks are present because they can have different origins. Fermi dyads are a common class of such doublets, stemming from the resonance of the fundamental excitation of a mode with the overtone of another. We present a new, efficient approach to unambiguously characterize Fermi resonances in density functional theory (DFT) based simulations of condensed phase systems. With it, the spectral features can be assigned and the two resonating modes identified. We also show how data from DFT simulations employing classical nuclear dynamics can be post-processed and combined with a perturbative quantum treatment at a finite temperature to include analytically thermal quantum nuclear effects. The inclusion of these effects is crucial to correct some of the qualitative failures of the Newtonian dynamics simulations at a low temperature such as, in particular, the behavior of the frequency splitting of the Fermi dyad. We show, by comparing with experimental data for the paradigmatic case of supercritical CO₂, that these thermal quantum effects can be substantial even at ambient conditions and that our scheme provides an accurate and computationally convenient approach to account for them. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4979199]

I. INTRODUCTION

Fermi resonances were first identified by Fermi in 1931¹ to explain the unexpected multiple peaks observed by Rasetti in the Raman spectrum of CO₂.^{2,3} Since then, they have been associated with double or multiple peak structures in the vibrational signature of many systems, such as organic molecules,^{4–8} carotenoid,⁹ water,^{10–13} or ammonia.^{14,15} Furthermore, Fermi resonances are also important in the context of energy transfer. In fact, they can dramatically influence relaxation processes after photoexcitation and the resulting chemical reactivity.^{16–18} This may originate, for example, the ultrafast vibrational energy transfer observed for water molecules at air interfaces.¹³

The unambiguous identification of Fermi resonances is, however, very challenging because multi-peak structures in the spectroscopic signature of a given system may have different origins. In particular, double (or multiple) peaks can stem either from a resonance or from the different environments that the probed molecular vibration feels. An example is the two peaks observed via spectroscopy studies of the structure and specific acidity of water/quartz interfaces for the O–H stretching.¹⁹ This splitting might correspond to two "states" of water,^{20,21} but the possibility of a Fermi resonance cannot be discarded.²²

Experimentally, the direct approach to discriminate if a resonance is present is isotopic substitution. However, this approach is often problematic because substituted compounds may not be readily available, in particular for large molecules, or because the relevant vibration, e.g., in liquid water, involves labile protons that can easily undergo exchanges with other available protons.

Given these experimental difficulties, full atomistic simulations should play a major role in the identification of Fermi resonances. In particular, DFT-based simulations have emerged in several cases as the computational tool of choice to investigate effectively the structure of complex systems.²³ In simulation, however, Fermi resonances have been mostly

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studied with other approaches. For example, by adopting generalized coordinates, which lead to kinetic energy coupling,^{24,25} by designing a coupled Hamiltonian that incorporates experimental information,^{26–29} or by using accurate but very expensive quantum chemistry methods.³⁰ Semi-classical methods,³¹⁻³⁴ combining an action-angle variable representation of the system with model Hamiltonians which explicitly incorporated couplings and resonances, have also proved powerful tools to interpret the spectra often with a state-to-state resolution of the peaks. These approaches included specific terms, e.g., non-harmonic contributions in the diagonal terms in the Hamiltonian, to account for features such as anharmonic shifts. In this family of methods, classical trajectories in curvilinear coordinates were also run on the model Hamiltonian to interpret the spectra in terms of a qualitative analysis of the orbits of the underlying dynamics.

In this work, we discuss instead to what extent fully atomistic Newtonian dynamics on a DFT potential surface can be used to characterize the Fermi dyad in supercritical CO₂. The advantage of such simulations, done in Cartesian coordinates on sufficiently accurate potential energy surfaces that implicitly but automatically contain all the anharmonicities and couplings of the system's modes, is that no model is imposed: if it exists, the resonance will manifest itself via a splitting of the Fourier transform of the velocity autocorrelation function, the microscopic observable corresponding to the experimental signal. When attempting to describe Fermi resonances with these simulations, however, at least three important questions must be addressed. First, the quality of the DFT description of the system must be assessed. Second, an accurate assignment of the modes originating the splitting in the power spectrum must be possible to unambiguously assign the feature to a Fermi resonance. Third, given that a fully classical description of the statistical properties and of the dynamics cannot capture correctly all the features of the resonances between the discrete quantum modes of the system, and that a full quantum description of the dynamics is beyond current computational possibilities for condensed phase DFTbased simulations, approximate tools to reinstate and compute some of the quantum features of the spectra must be developed.

Let us begin by considering the first question. Recent work³⁵ showed that full atomistic DFT-based simulations can be used to study the Fermi dyad in supercritical CO₂, providing results in good agreement with experiments. Crucially, this work proves that, in spite of the approximations in the electronic structure calculation, DFT models effectively the coupling between the symmetric CO stretching and the bending. In particular, the DFT fundamental frequencies for these modes are in the 1:2 ratio without which the resonance cannot be observed. The focus of this work was twofold: to determine the effect of the isotopic substitution of O on the order and intensity of the peaks in the Fermi dyad and to assess the nature of this doublet. Ref. 35 is the first example in the literature in which full atomistic DFT simulations were used to investigate in detail Fermi resonances in supercritical CO₂. In fact, while previous simulations^{36,37} had correctly characterized the structure and dynamics of the system, the possible origin of the splitting observed in the symmetric stretch

band from a resonance was mentioned but not investigated in detail.

In the present paper, we then reconsider the Fermi resonance in supercritical CO₂ analyzing and complementing the results of DFT-based classical molecular dynamics (MD) with two new tools that target questions two and three above. The first tool, mode localization, makes it possible to refine the peak assignment to specific atomic motions. Mode localization, in its different flavors, has been proposed to solve the problem of unambiguous band assignment, but so far it is limited to the interpretation of fundamental bands.^{38–41} Here, we extend this approach to the analysis of anharmonic combination bands such as Fermi resonances. Our approach includes the degeneracy of the bending mode in the assignment procedure. This feature was ignored in Ref. 35 and, as discussed in Section III B, this leads to a misleading interpretation of the resonance. The second tool that we use, quantum perturbation theory, makes it possible to capture correctly the behavior of the Fermi dyad splitting with temperature. As discussed more in detail in the following, to allow for a coherent comparison of experimental data, in which the Fermi resonance at higher temperatures has multiple peaks corresponding to increasingly thermally excited discrete resonances, and simulations, in which the classical dynamics can only produce two broad peaks in the resonance, this splitting is defined as the distance between the first moment of the power spectrum of the left and right shoulders of the Fermi dyad. In Section II B, it is shown that the classical evolution of the nuclei predicts a monotonically decreasing amplitude of the splitting with temperature, with zero splitting at zero temperature in the case of perfect resonance. This result is qualitatively wrong due to zero point energy effects that cause the decrease to saturate as the temperature decreases and maintain a finite splitting at zero temperature. Brute force quantum simulations to account for them are, however, problematic for a realistic representation of this condensed phase system. In the following, we then adopt an alternative strategy. In Section II B, an analytic formula for the Fermi resonance splitting as a function of temperature is obtained, using quantum perturbation theory on the model Hamiltonian originally proposed by Fermi, to evaluate the short time evolution of a suitable correlation function. When appropriately combined with data from the classical DFT-based simulation, this formula makes it possible to correct the splitting calculated via classical molecular dynamics with essentially no increase in the cost. Comparison with experimental data at three different temperatures and pressures shows that this procedure is very effective. Note that previous DFT-based simulations of the system completely neglected nuclear quantum effects. In contrast, our approach complements fully classical nuclear propagation on a DFT based potential, with a quantum correction procedure. As explained more in detail in the following, this perturbative approach makes it possible to account for quantum thermal effects such as the zero point energy and the correct sampling of excited vibrational states at a finite temperature. Of course, since the time evolution of the system remains Newtonian, dynamical quantum effects, such as coherence, are beyond the scope of this work. These dynamical effects, however, are not relevant for the calculation of the splitting as a

function of temperature, as demonstrated by the comparison with experiments.

Supercritical CO₂ was chosen as a reference system because (i) it is well known that the double peak in CO₂ is originated from a Fermi resonance and (ii) DFT-based simulations are able to reproduce this feature, meaning that the stretching and bending frequencies are correctly on resonance, as already reported in the literature.^{35–37} Given these properties, this is the ideal system to demonstrate the reliability and efficiency of the two analysis tools introduced in this work. These tools, however, do not depend on a specific system and can be applied to investigate Fermi resonances whenever a sufficiently accurate DFT-based simulation is available, anharmonicity and coupling among the resonant modes are not too strong allowing for a perturbative treatment, and the relevant quantum effects are mostly thermal in origin (zero point energy and quantum fluctuations effects).

II. THEORY

In this section, the two new tools to characterize Fermi resonances at a finite temperature are introduced. The first starts from a previously developed mode localization method³⁸ and extends it to include overtones. This mode localization analysis acts on the data obtained directly from the DFT-based trajectory. The second starts from an effective Hamiltonian model for the system and applies quantum perturbation theory to derive an analytic correction to the temperature behavior of the splitting of the Fermi dyad that accounts for nuclear quantum effects. The model contains one input parameter (in addition to the effective frequencies of the modes) that can be obtained either from the classical DFT-based simulation or from experiments.

A. Mode localization including overtones and couplings

Let us begin by summarizing the mode localization methods used as the starting point for our developments. Consider a set of *n* coordinates $\mathbf{q}(t) = (q_1(t), \ldots, q_n(t))$ and their derivatives $\dot{\mathbf{q}}(t) = (\dot{q}_1(t), \ldots, \dot{q}_n(t))$ as obtained along a Newtonian trajectory in a molecular dynamics, possibly DFT-based, simulation. From the Fourier transform of the self-correlation and cross correlation functions of the derivatives, we construct the matrix $\mathbf{P}^q \equiv (P_{ii}^q)$, with

$$P^{q}_{ij}(\omega) = \int_{-\infty}^{+\infty} \langle \dot{q}_i(0)\dot{q}_j(t)\rangle e^{i\omega t} dt.$$
(1)

The diagonal elements of this matrix are the power spectrum of each coordinate q_i and are in general delocalized in frequency, contributing to multiple peaks. We then look for a linear transformation of the initial coordinates $\mathbf{q}(t)$ into modes $\mathbf{z}(t) = (z_1(t), \dots, z_n(t))$,

$$z_i(t) = U_{ij}q_j(t), \tag{2}$$

such that the power spectra of these new modes are as localized as possible in the frequency space. The transformation matrix that satisfies this requirement, $\mathbf{U} \equiv (U_{ij})$, is such that the quantity

$$\sum_{i} \left[\int_{-\infty}^{+\infty} \omega^4 P_{ii}^z(\omega) \, d\omega - \left(\int_{-\infty}^{+\infty} \omega^2 P_{ii}^z(\omega) \, d\omega \right)^2 \right] \quad (3)$$

is minimal with the constraint

$$\int_{-\infty}^{+\infty} P_{ij}^{z}(\omega) \, d\omega = \delta_{ij}. \tag{4}$$

In the equations above, the matrix \mathbf{P}^z is constructed from the modes $\mathbf{z}(t)$ in analogy with Eq. (1). This minimization problem is easily solved using linear algebra.³⁸

The method just described amounts to looking for an optimal harmonic approximation to describe the dynamics of the system.³⁸ To go beyond and describe non-harmonic couplings with overtones, as for the Fermi resonance, we first note that if a mode $\dot{z}_j(t)$ has a very localized spectrum around a frequency ω_j , the quantity $z_j(t)\dot{z}_j(t)$ oscillates at a frequency $2\omega_j$ and represents the overtone of mode *j*. Thus, starting from the set of effective mode derivatives $\dot{\mathbf{z}}(t) = (\dot{z}_1(t), \dots, \dot{z}_n(t))$, we extend this set by including terms of the form $z_j(t)\dot{z}_j(t)$ to generate an initial set $\dot{\mathbf{s}} = (\dot{s}_1(t), \dots, \dot{s}_{n+m}(t))$,

$$\begin{cases} \dot{s}_i(t) = \dot{z}_i(t) & \text{for } 1 \le i \le n, \\ \dot{s}_i(t) = z_{j_i}(t)\dot{z}_{j_i}(t) & \text{for } n < i \le n+m, \end{cases}$$
(5)

where the indices j_i indicate the modes whose overtones are considered. From this extended set of coordinates, we apply the localization procedure described above to transform the set of coordinates $\dot{\mathbf{s}}$ to modes $\dot{\mathbf{y}}(t)$ via a linear transformation

$$\dot{y}_i(t) = V_{ij}\dot{s}_j(t). \tag{6}$$

Relevant physical information can be extracted from the localized modes. In particular, we compute the frequency of each mode as the average frequency over their power spectrum $P_{ii}^{y}(\omega)$,

$$\omega_i = \frac{\int_0^\infty \omega P_{ii}^y(\omega) \, d\omega}{\int_0^\infty P_{ij}^y(\omega) \, d\omega}.\tag{7}$$

Note that these frequencies are in fact effective frequencies, containing implicitly anharmonic effects, since they are extracted from a molecular dynamics simulation done on the fully anharmonic, possibly DFT-based, Hamiltonian for the atoms.

Furthermore, the contributions of the modes $\dot{\mathbf{s}} \equiv (\dot{s}_1(t), \dots, \dot{s}_{n+m}(t))$ in the resulting modes $\dot{\mathbf{y}} \equiv (\dot{y}_1(t), \dots, \dot{y}_{n+m}(t))$ is evaluated from the normalisation condition (4), which can be rewritten as

$$\langle \dot{y}_i \dot{y}_i \rangle = V_{ij} V_{ik} \langle \dot{s}_j \dot{s}_k \rangle = 1.$$
(8)

The contribution $w_{j\rightarrow i}$ of the mode \dot{s}_j in the mode \dot{y}_i can be then defined as the sum

$$w_{j\to i} \equiv \sum_{k} V_{ij} V_{ik} \langle \dot{s}_j \dot{s}_k \rangle \tag{9}$$

or more simply as the diagonal term

$$w_{i \to i} \equiv V_{ij} V_{ij} \langle \dot{s}_j \dot{s}_j \rangle. \tag{10}$$

In the present case, the modes $\dot{\mathbf{s}} \equiv (\dot{s}_1(t), \dots, \dot{s}_{n+m}(t))$ are already orthogonal, since they were obtained from a prior mode localization, such that only the diagonal terms remain in Eq. (9) and the definitions above are equivalent.

The localization procedure for determining effective normal modes described above works even for systems with substantial anharmonicities and large bands (see, for example, applications to N-methyl-acetamide³⁸ or peridinine⁴²). Anharmonic effects can, however, lead to a broadening of bands and, when this occurs, it is expected that the $z_j(t)\dot{z}_j(t)$ terms may also not be (well) localized. Although an *a priori* assessment of the convergence of the procedure is problematic, to overcome this problem, higher terms in the localizations could be included by expanding the basis of functions in Eq. (5), e.g., including general terms as derivatives of successive products of z_i . This, however, goes beyond the aim and the needs of this paper since in the case considered here the localization was successful with the basis introduced above.

B. Perturbative quantum treatment at finite temperature for a model Hamiltonian

To develop an approximate method to reinstate some of the quantum properties of Fermi resonances in CO₂, we proceed in two steps. These steps are analytical and, as such, do not require further simulations. However, they require input parameters that are obtained by post-processing data from the Newtonian DFT-based calculations or directly from experiments. In the first step, we adopt the simplified description of the phenomenon originally proposed by Fermi,¹ by introducing an effective Hamiltonian for the resonant modes. This Hamiltonian is composed by a diagonal (H^0) and a coupling (H^P) term,

$$H^{0} = \frac{p_{x}^{2}}{2m_{1}} + \frac{p_{\xi}^{2}}{2m_{2}} + \frac{p_{\eta}^{2}}{2m_{2}} + \frac{1}{2}m_{1}\omega_{1}^{2}x^{2} + \frac{1}{2}m_{2}\omega_{2}^{2}(\xi^{2} + \eta^{2}),$$
(11)
$$H^{P} = \frac{1}{2}\gamma_{12}x(\xi^{2} + \eta^{2}).$$

All momenta and coordinates above are operators: x is the high frequency mode describing the symmetric stretch in CO₂, and ξ and η are the two degenerate low frequency bending modes. m_1 , ω_1 and m_2 , ω_2 are their respective masses and effective harmonic frequencies. γ_{12} is the coupling parameter, that, in our perturbative treatment, will be assumed to be small. We also assume that in the range of pressures considered, the fundamental frequencies ω_1 and ω_2 are constant. Note that in other models for Fermi resonances, H_0 may not be simply harmonic,^{31–34} but, for example, the potential for the stretch may be chosen as a Morse potential to capture anharmonic shifts in the experiments. However, since the values of our effective harmonic frequencies are obtained either from DFT-based molecular dynamics done in Cartesian coordinates on a potential energy surface which directly has the anharmonicities, or from experiments, these shifts are automatically incorporated in our model.

In the second step of our approximate scheme, we characterize the dyad and its behavior by choosing, in analogy with the classical case, see Eq. (5), appropriate combinations of three internal dynamical quantities that generate excitation of the *x* mode and the overtones of ξ and η modes. Denoting by a_1^{\dagger} the creation operator for *x*, and by a_2^{\dagger} and a_3^{\dagger} the creation operators for ξ and η , we define

$$\mathcal{A}_{1}^{\dagger} = \omega_{1}x - i\frac{p_{x}}{m_{1}} = \sqrt{\frac{2\hbar\omega_{1}}{m_{1}}}a_{1}^{\dagger},$$

$$\mathcal{A}_{2}^{\dagger} = \left(\omega_{2}\xi - i\frac{p_{\xi}}{m_{2}}\right)^{2} = \frac{2\hbar\omega_{2}}{m_{2}}a_{2}^{\dagger}a_{2}^{\dagger},$$

$$\mathcal{A}_{3}^{\dagger} = \left(\omega_{2}\eta - i\frac{p_{\eta}}{m_{2}}\right)^{2} = \frac{2\hbar\omega_{2}}{m_{2}}a_{3}^{\dagger}a_{3}^{\dagger}.$$
(12)

In the absence of coupling, the correlation function $\langle A_1 A_1^{\dagger}(t) \rangle$ oscillates at pulsation ω_1 , the high frequency, while $\langle A_2 A_2^{\dagger}(t) \rangle$ and $\langle A_3 A_3^{\dagger}(t) \rangle$ oscillate at $2\omega_2$, corresponding to the overtone of the low frequency. The cross correlations of this set of operators are all equal to zero by construction. In these conditions, the power spectra associated with these correlation functions are perfectly localized delta distributions. When the coupling is turned on, the modes mix and a doublet of bands appears.

To decompose the doublet, we start from the operators A_i^{\dagger} and proceed, again in analogy with the classical case, to construct new operators with maximally decorrelated spectra. To illustrate how, let us consider a set of generic operators Y_i . At short times

$$\langle \mathcal{Y}_{i} \mathcal{Y}_{j}^{\dagger}(t) \rangle \equiv \langle \mathcal{Y}_{i} \mathcal{Y}_{j}^{\dagger}(0) \rangle + \langle \mathcal{Y}_{i} \dot{\mathcal{Y}}_{j}^{\dagger}(0) \rangle t + \mathcal{O}(t^{2})$$

$$\equiv \langle \mathcal{Y}_{i} \mathcal{Y}_{j}^{\dagger} \rangle + \frac{i}{\hbar} \langle \mathcal{Y}_{i}[H, \mathcal{Y}_{j}^{\dagger}] \rangle t + \mathcal{O}(t^{2}).$$
(13)

Based on the expression above, it is possible to obtain linear combinations of the A_i , i = 1, 2, 3, operators that are fully decorrelated up to first order in time. This is done by solving the generalized eigenvalue problem

$$\mathcal{H}\boldsymbol{c} = (\mathcal{S}\boldsymbol{c})\hbar\boldsymbol{\omega} \tag{14}$$

with the condition

$$\boldsymbol{c}^{\dagger} \boldsymbol{\mathcal{S}} \boldsymbol{c} = \boldsymbol{1}, \tag{15}$$

where **1** is the 3×3 unit matrix. \mathcal{H} and \mathcal{S} are matrices with elements

$$\mathcal{H}_{ij} = \langle \mathcal{A}_i[H, \mathcal{A}_j^{\dagger}] \rangle,$$
$$\mathcal{S}_{ij} = \langle \mathcal{A}_i \mathcal{A}_j^{\dagger} \rangle,$$

and ω is a diagonal matrix where each element represents a frequency. From the 3 × 3 matrix $c \equiv (c_{ij})$, we construct new operators $\mathcal{B}_j = \sum_i c_{ji} \mathcal{A}_i$ such that

and

$$\langle \mathcal{B}_i \mathcal{B}_j^{\dagger} \rangle = \delta_{ij} \tag{16}$$

$$\frac{i}{\hbar} \langle \mathcal{B}_i[H, \mathcal{B}_j^{\dagger}] \rangle = i\omega_i \delta_{ij}.$$
(17)

The interpretation of Eq. (16) is that the excitations induced by the operators \mathcal{B}_i are uncorrelated at equilibrium. Furthermore, the first moments over the power spectra of the operators \mathcal{B}_i are equal to $\frac{1}{\hbar} \langle \mathcal{B}_i[H, \mathcal{B}_i^{\dagger}] \rangle$. Equation (17) then directly relates the first moments ω_i to, time independent, quantum thermal average quantities. Finally, the fact that the matrix *c* solves Eq. (14), means that these frequencies are as distant as possible from each other. Thus, the power spectra of the operators \mathcal{B}_i have minimal overlap and are maximally localized. To determine, to first order in γ_{12} , the matrix elements of \mathcal{H} and \mathcal{S} , we use the Kubo formula⁴³

$$e^{-\beta(H^{0}+H^{P})} = e^{-\beta H^{0}} - \int_{0}^{\beta} d\lambda \{e^{-\beta H^{0}} e^{\lambda H^{0}} H^{P} e^{-\lambda(H^{0}+H^{P})}\}$$

 $(\beta = 1/k_BT)$, where k_B is Boltzmann's constant and T the temperature) to obtain the following expressions of \mathcal{H} and \mathcal{S} :

$$\mathcal{H}_{ij} \simeq Tr\{e^{-\beta H^0} \mathcal{A}_i[H^P, \mathcal{A}_j^{\dagger}]\} - \int_0^\beta d\lambda Tr\{e^{-\beta H^0} e^{\lambda H^0} H^P e^{-\lambda H^0} \mathcal{A}_i[H^0, \mathcal{A}_j^{\dagger}]\}$$
(18)

and

$$S_{ij} \simeq Tr\{e^{-\beta H^0} \mathcal{A}_i \mathcal{A}_j^{\dagger}\} - \int_0^\beta d\lambda Tr\{e^{-\beta H^0} e^{\lambda H^0} H^P e^{-\lambda H^0} \mathcal{A}_i \mathcal{A}_j^{\dagger}\}.$$
 (19)

Given the form of the Hamiltonian and of the operators \mathcal{A}_i^{\dagger} , analytic expressions for the matrix elements can be obtained. These expressions are explicit functions of β , γ_{12} , via H^P , and of the unperturbed frequencies and masses of the modes, via \mathcal{A}_i^{\dagger} . For a given system, the only unknown parameter required for their calculations is γ_{12} . As we will show, this parameter can be estimated starting from the classical splitting and fed back to the equations above to obtain the quantum correction. The details of these calculations are given in the Mathematica spreadsheet in the supplementary material. Here we report the results for the reader's convenience. First of all, observe that both \mathcal{H} and \mathcal{S} are symmetric matrices. Furthermore, permutation symmetry of the two bending modes implies that

$$S_{12} = S_{13}, \quad S_{22} = S_{33}, \quad S_{23} = 0$$
 (20)

with analogous results for the matrix elements of \mathcal{H} . Finally, explicit calculation shows that all matrix elements depend on the coupling term via the quantity $\chi_{12} = \gamma_{12}/(\sqrt{m_1}m_2)$ that will be used from now on. The expressions for the non-trivial matrix elements are

$$S_{11} = \frac{2e^{\beta\hbar\omega_1}\hbar\omega_1}{m_1(e^{\beta\hbar\omega_1} - 1)},\tag{21}$$

$$S_{12} = -\chi_{12} \frac{\hbar^2}{4\sqrt{m_1}m_2} \sinh^{-1} \left[\frac{\beta\hbar\omega_1}{2}\right] \sinh^{-1} \left[\frac{\beta\hbar\omega_2}{2}\right]^2 \times \frac{\sinh\left[\frac{1}{2}\beta\hbar(\omega_1 - 2\omega_2)\right]}{\omega_1 - 2\omega_2},$$
(22)

$$S_{22} = \frac{8e^{2\beta\hbar\omega_2}\hbar^2\omega_2^2}{\left(e^{\beta\hbar\omega_2} - 1\right)^2 m_2^2}$$
(23)

and

$$H_{11} = \hbar \omega_1 S_{11},$$
 (24)

$$H_{12} = \chi_{12} \frac{\hbar^3 \left(-\omega_2 + \Delta \coth\left[\frac{\beta \hbar \omega_2}{2}\right]\right)}{2\sqrt{m_1}m_2(\omega_1 - 2\omega_2)}$$
(25)

with

$$\Delta = \left(\omega_1 - 2\omega_2 + \omega_1 \coth\left[\frac{\beta\hbar\omega_1}{2}\right] - \omega_2 \coth\left[\frac{\beta\hbar\omega_2}{2}\right]\right)$$

and

$$H_{22} = 2\hbar\omega_2 S_{22}.$$
 (26)

Given the expressions above, the eigenvalues ω_i and consequently the value of the splitting $\Delta \omega$ are calculated by solving the secular equation, Eq. (14). Explicit, but involved, expressions for these quantities are given in the Mathematica notebook in the supplementary material. In the rest of this section, we shall consider two limits of the perturbative treatment discussed above from which relevant physical information can be obtained.

Let us consider first the classical limit, obtained by letting $\hbar \rightarrow 0$ in the matrix elements of S and H. This limit provides us with a consistent way to connect the quantum perturbative approach with the DFT-based simulations in which classical statistic and dynamics are employed. In particular, the classical limit for the value of the splitting, which contains χ_{12} , will be used as the basis of our estimate for this parameter. The classical limit of the matrix elements will also make it possible to discuss the zero temperature behavior of the Fermi splitting in a purely classical description of the dynamics. As shown in the supplementary material, the classical limit of the nontrivial matrix elements is

$$S_{11} = \frac{2}{\beta m_1},$$
 (27)

$$S_{12} = -\chi_{12} \frac{1}{\beta^2 \sqrt{m_1} m_2 \omega_1 \omega_2^2},$$
 (28)

$$S_{22} = \frac{8}{\beta^2 m_2^2}$$
(29)

and

$$H_{11} = \hbar \omega_1 S_{11}, \quad H_{22} = 2\hbar \omega_2 S_{22}, \quad H_{12} = 0.$$
 (30)

Using the results above, the classical limit of the splitting to first order in χ_{12} is

$$\Delta\omega_{cl}(T) = \sqrt{\frac{k_B T \chi_{12}^2}{\omega_1 \omega_2^3} + (\omega_1 - 2\omega_2)^2}.$$
 (31)

The classical splitting can also be obtained as an output of the (classical) DFT-based MD of the system. Using the value computed from the simulations and inverting the equations above, then, provides an estimate of the parameter χ_{12} for the off-resonance and perfect resonance case. This estimate can be fed back in the quantum perturbation formulae to obtain the splitting of the Fermi dyad as a function of the other parameters, e.g., temperature.

Note that, in the case of perfect resonance, $\omega_1 = 2\omega_2$, the splitting is given by

$$\Delta\omega_{cl}^{res} = \frac{2\sqrt{2k_BT}}{\omega_1^2}\chi_{12}.$$
(32)

and exhibits a \sqrt{T} dependence as a function of temperature. This implies, in particular, that the splitting will vanish at zero temperature in the limit of perfect resonance. This can be understood as follows. Semiclassically, the Fermi splitting is due to the modulation of the force acting on the symmetric stretch, proportional to $(\xi^2 + \eta^2)$, which oscillates at $2\omega_2$. The amplitude of this modulation is governed by the amplitude of the fluctuations of the two low frequency modes. At a finite temperature, these fluctuations are finite leading to a non-zero splitting and explaining how a classical simulation can capture the phenomenon of the Fermi resonance. However, when $T \rightarrow 0$, so do the classical fluctuations leading to the absence of classical splitting in this limit.

The zero temperature behavior of the classical splitting just described, however, is qualitatively wrong and, as shown in Sec. IV, for CO₂ leads to discrepancies with experiments even at room temperature. In fact, the same description as above for the first moment of the two multiplets of the Fermi dyad, but in a quantum framework, indicates that at zero temperature, zero point energy effects will maintain finite amplitude oscillations, and therefore non-zero splitting, for the quantum Fermi resonator. This argument can be made more precise by considering the splitting obtained by computing the matrix elements of S and H as $T \rightarrow 0$. In this limit, we have (see the supplementary material)

$$S_{11} = \frac{2\hbar\omega_1}{m_1}, \quad S_{12} = 0, \quad S_{22} = \frac{8\hbar^2\omega_2^2}{m_2^2},$$
 (33)

$$H_{11} = \hbar \omega_1 S_{11}, \quad H_{22} = 2\hbar \omega_2 S_{22}, \quad H_{12} = \frac{\chi_{12} \hbar^3}{\sqrt{m_1 m_2}}$$
(34)

from which the zero temperature quantum expression of the Fermi splitting is obtained,

$$\Delta \omega^* = \sqrt{\frac{\chi_{12}^2 \hbar}{2\omega_1 \omega_2^2} + (\omega_1 - 2\omega_2)^2}.$$
 (35)

We shall see in Sec. IV that, with the value of χ_{12} obtained from the classical DFT-MD, the expression above provides an excellent estimate of the splitting for CO₂ at T = 0 as extrapolated from experiments. More in general, our temperature analysis (using the expression for the splitting calculated as discussed here and shown in the supplementary material) indicates that molecular dynamics for classical nuclei will underestimate the splitting for low temperatures. The definition of "low temperature" will, of course, vary depending on the system and on the interplay between the coupling strength and the values of the unperturbed frequencies of the resonating modes.

Let us conclude this section with some comments on the strengths and limits of the proposed approach. First, we have chosen the simplest model Hamiltonian which can be used to post-process the Newtonian simulation data (in the present case, they are DFT-based molecular dynamics) and restore, approximately, some quantum nuclear effects. Note that, although our model does not include explicitly diagonal anharmonicities, the frequencies used in Eq. (11) are in fact effective frequencies obtained, for example, from DFT-based simulations (via Fourier transform of the velocity-velocity correlation function on the DFT anharmonic potential). Therefore these frequencies include anharmonic effects. In this sense, the model is inspired by the procedure followed in spectroscopic interpretations in which the harmonic frequencies are first shifted for anharmonic effects and then the coupling is turned on.⁴⁴ Furthermore, to limit as much as possible the number of parameters to be obtained combining the simulations and the model, we have chosen a description in which

the only parameter other than the effective frequencies is γ_{12} . In spite of its simplicity, this Hamiltonian has proved effective for CO₂^{1,44,45} but also for other systems like peridinin,⁹ CS₂,⁴⁶ thioacetamide and methylthiourea,⁴⁷ aniline,⁷ or ammonia.¹⁴ Furthermore, as reported by Sibert *et al.*²⁴ the choice between the different forms of Hamiltonians with the Fermi coupling as a potential energy or as a kinetic energy term is *"solely one of perspective."* Indeed it amounts to a choice of rectilinear vs curvilinear coordinates. As they reported, *"at this level the curvilinear and rectilinear approaches are of comparable accuracy."* The obvious advantage of the chosen model Hamiltonian is that all the integrals required to compute the matrix elements in the perturbation treatment at a finite temperature can be performed analytically.

Second, our formal developments rely on two approximations: a short time description of the properties of the time correlation function, see Eq. (13), and perturbation theory valid to first order in γ_{12} . The second approximation will fail for systems with strong anharmonic couplings. The first limits, among other things, the quantum observables that we can attempt to describe with reasonable accuracy. As shown in Eq. (17), short time accuracy is, however, enough to estimate the value of the first moment of the power spectrum of the localized modes, the quantity that we focus on in this work. Note that, when computing exactly this average value, the contribution of different discrete quantum levels appears as a weight for a continuous observable. These discrete weights are, of course, not accessible in our simulation which samples instead the (continuous) classical thermal distribution generated by the Newtonian dynamics plus thermostat on the full DFT-based potential. The perturbative treatment provides, however, a correction procedure for the average which reinstates some of the properties of the quantum thermal distribution. (See also the discussion at the end of Section IV A.)

III. MATERIALS AND METHODS

A. Density functional based molecular dynamics simulations

We performed density functional based Born-Oppenheimer molecular dynamics (DFT-MD) simulations using the software CP2K⁴⁸ and in particular the Quickstep algorithm.⁴⁹ The latter employs a hybrid Gaussian plane-wave (GPW) method.⁵⁰ We use the Goedecker-Teter-Hutter (GTH) normconserving pseudo-potentials⁵¹⁻⁵³ to replace the core electrons. We cut off the electronic density at 400 Ry and used NN50 smoothing for applying the exchange-correlation potential on the real space grid. For C and O atoms, we use a triple-zeta valence doubly polarised (TZV2P) basis set.⁵⁴ The exchange-correlation interactions are taken into account by the gradient-corrected BLYP functional.^{55,56} We add dispersive interaction corrections by using the DFT-D3 scheme,⁵⁷ with a cutoff of 15 Å. The simulations were performed with 128 CO₂ at a constant volume with the densities taken from the NIST database⁵⁸ so as to match the experimental pressures. These densities are $\rho = 0.7 \text{ g cm}^{-3}$ for T = 315 K and P = 120 bars, while $\rho = 0.56 \text{ g cm}^{-3}$ for both simulations at T = 550K and P = 660 bars and T = 773 K and P = 1160 bars. The temperature was held fixed using a chain of four Nose-Hoover

thermostats and the Yoshida algorithm⁵⁹ with a characteristic time set to 2.4 ps. The time step for the Born-Oppenheimer dynamics was $\delta t = 2$ fs and the total integration time was 40 ps. The initial conditions were generated from long MD trajectories using the MSM3 force-field.⁶⁰

B. Definition of internal modes for CO₂ from molecular dynamics trajectories

The four internal modes of CO_2 are shown in Figure 1 for the reader's convenience. They are the asymmetric and symmetric stretching plus two degenerate bendings (in *xz* and *yz* planes following our reference system).

The degeneracy of the two bending modes poses a difficulty when extracting the dynamics of the internal modes for a linear molecule such as CO₂ from a molecular dynamics simulation. Commonly, if we define an internal mode to be a bend θ between three atoms, A, B, C, with B the central atom, the bend will be extracted from a molecular simulation trajectory as the angle between the vectors \vec{BA} and \vec{BC} taken to be in the interval $[0, \pi]$,

$$\theta = \operatorname{acos} \frac{\vec{BA} \cdot \vec{BC}}{\|\vec{BA}\| \cdot \|\vec{BC}\|}.$$
(36)

However, only one such bend can be defined instead of two that are necessary when A, B, and C are aligned. Around the linear geometry, these two modes are bending motions in two orthogonal planes that contain the atoms A, B, and C, as in the bottom part of Figure 1. If these two planes are taken arbitrarily along the molecular simulation trajectory, this may lead to



FIG. 1. Schematic representation of internal modes of CO_2 . The molecule lies on the *z* axis, such that the two (degenerate) bending modes are in *xz* and *yz* planes.

spurious dynamics of the two bends. To avoid this problem, we define the two internal bending modes with respect to a molecular frame uniquely defined along the dynamics (barring a choice made for the initial configuration). The molecular frame is defined by considering, at each step of the simulation the Eckart frame⁶¹ of the CO₂ molecule. The \vec{Z} axis is taken as the unitary vector along the reference CO₂ molecule used to define the instantaneous Eckart frame. Then the \vec{X} and \vec{Y} vectors are two orthogonal unit vectors both orthogonal to \vec{Z} defined such that the rotation that transforms the frame $\vec{X}\vec{Y}\vec{Z}$ at time $t - \delta t$ to the frame $\vec{X}\vec{Y}\vec{Z}$ at time t has no component along the \vec{Z} axis.

Given this instantaneous molecular frame, we define the four internal modes as follows. r_1 and r_2 are the two CO distances and θ_X , θ_Y are taken as the angles of the projections of the two CO vectors on the planes that contain the center of mass and the vectors \vec{X} , \vec{Z} and \vec{Y} , \vec{Z} , respectively. These two vectors are now taken to be in the interval $[-\pi, \pi]$ since the *XZ* and *YZ* planes are oriented by the two vectors that define them.

It will be shown in Sec. IV that this choice of the reference frame leads to two modes whose spectrum is well localized at the expected CO_2 bend frequency and is indeed degenerate. Performing mode localization starting from the coordinates r_1, r_2, θ_X , and θ_Y leads to 4 effective normal modes that correspond to the CO₂ symmetric and antisymmetric stretches while the two modes θ_X and θ_Y are left unchanged by symmetry. Since this set of modes is unable to unambiguously assign the origin of the peaks in the Fermi dyad, we then repeat the mode localization using as a basis the set of 6 coordinates obtained by adding to the four modes indicated above the quantities $\theta_X(t)\dot{\theta}_X(t)$ and $\theta_Y(t)\dot{\theta}_Y(t)$, as discussed in Section II A. In Sec. IV we show that with this extended set both peaks of the dyad are assigned to a unique mode. For the simplicity of notation, in the following we return to the lower case notation, e.g., θ_x , to indicate the bending modes, but these are calculated in the molecular frame just described.

C. Perturbative calculations

The analytical expressions of the matrix elements of matrices \mathcal{H} and \mathcal{S} (from which Equations (21)–(26) were derived), as well as the $\hbar \to 0$ and $T \to 0$ limits and the solutions of the generalized eigenvalue equation, Eq. (14), were obtained using the Mathematica⁶² software. The notebook for the calculation of these terms is provided in the supplementary material.

D. Raman experiments

The experimental spectra were obtained using the highpressure high-temperature setup of the Neel Institute (Grenoble, France).⁶³ This setup was designed to integrate an autoclave in the Raman spectrometer setup. We used the green wavelength of an Ar laser ($\lambda = 514.5$ nm) from Spectra Physics (Stabilite 2017) and a T64000 Raman spectrometer from Jobin-Yvon. The Raman spectrometer was calibrated using the N₂ gas peak (2332 cm⁻¹) at room-temperature and ambient pressure. The spectra were recorded using a 1800 grooves mm⁻¹ grating on the 1200–1500 cm⁻¹ range and the background arising mainly from the windows of the autoclave was removed. Sapphire cell and pistons (with silicon o-ring) were used for the sample. The cell was charged with CO₂ dry ice, the cell being immersed in liquid nitrogen to maintain the CO₂ solid during the loading phase in the autoclave. Measurements were repeated twice to ensure the reproducibility of the spectra. The Fermi splitting was determined by taking the difference between the value of the center of mass of the spectra in the range $\omega \in [1200, 1325]$ cm⁻¹ for the lowest frequency and $\omega \in [1325, 1500]$ cm⁻¹ for the highest. In this way, it is possible to obtain average peak positions and one splitting value for each temperature. This average value gives us an observable which can be compared to results obtained from DFT-based simulations (in which by definition the peaks are a thermal average over a Newtonian dynamics) and to our thermal average quantum treatment.

IV. RESULTS

A. DFT-based classical molecular dynamics of CO₂

Figure 2 shows the vibrational density of states (VDOS) obtained from our DFT-based MD simulations of supercritical CO₂ at three different temperatures and pressures. Peaks appear in proximity of the frequencies of the bending mode around 630-635 cm⁻¹, of the symmetric stretch around 1260 cm⁻¹ (a low frequency component at 1211- 1253 cm^{-1} and a high frequency one at $1311-1328 \text{ cm}^{-1}$), and of the antisymmetric stretch around 2250-2273 cm⁻¹. The peak around 1260 cm⁻¹ is split into two components, a putative Fermi dyad, which are seen to evolve as a function of temperature and pressure. As reported previously,³⁵ Newtonian dynamics based on DFT are able to correctly describe a resonance in the region of the Fermi dyad at particular temperatures. We observe some small differences in the peak position with respect to this previous work: their peaks at 315 K are at 632, 1236, 1335, and 2315 cm⁻¹, while our simulations provide at 315 K peaks at 638, 1253, 1311, and 2273 cm⁻¹. The differences can originate from different details in the molecular dynamics: we used the BLYP functional, while Windisch et al.³⁵ used PBE functional, we used



FIG. 2. Vibrational density of states, from DFT-MD simulations at different temperatures and pressures. Black curve: T = 315 K, P = 120 bars; orange curve: T = 550 K, P = 660 bars; red curve: T = 773 K, P = 1160 bars.

a larger energy cutoff for plane-wave expansion (400 Ry vs 350 Ry), we have 128 CO₂ molecules, while in the previous study only 32 CO₂ molecules were considered, and we run for 40 ps, while the previous work reports simulation times of 20 ps. The differences between the functionals are relatively small and they both catch the key experimental findings, validating the adopted DFT model.

As discussed earlier, one difficulty in extracting individual vibrational modes of CO_2 is the presence of two bendings. Figure 3(a) reports the power spectrum of the symmetric and asymmetric stretches and of a single bending defined simply as the OCO angle. It clearly appears that this simple definition leads to a mode that has no contribution in the true bending region around 630 cm⁻¹ but on the contrary has its main contribution in the region of the overtone of bending.

The assignment of the peaks in Ref. 35 was performed by analyzing the spectrum of the velocity autocorrelation function. This quantity was first projected along the symmetric stretch mode, and the contribution of the (single) bending mode included in the calculation was then determined by subtraction. In the following, we show how a more detailed understanding of the nature of the different peaks can be obtained via the mode localization procedure introduced in this work. To that end, we begin by considering the localized power spectra computed from the four internal normal modes: r_1 , r_2 (CO distances), and θ_x , θ_y (bendings) introduced as the minimal set in Section III B. This power spectrum, at T = 300 K, is reported in Figure 3(b). The peaks corresponding to the Fermi dyad in the vibrational density of state shown in Figure 2 are broader than the reconstructed power spectrum of the internal effective normal modes in Figure 3(b), due to the broadening induced by the rotation of the CO₂ molecule.

As expected, two degenerate modes are observed at $\omega_b = 634 \text{ cm}^{-1}$ These are the original two bends θ_x and θ_y . The peak at $\omega_{as} = 2271 \text{ cm}^{-1}$ is attributed to the asymmetric stretch $r_1 - r_2$ and the double peak features at around $\omega_s = 1260 \text{ cm}^{-1}$ to the symmetric stretch $r_1 + r_2$.



FIG. 3. Results of DFT-MD simulation at 300 K. Panel (a): power spectra of the OCO angle and the symmetric and asymmetric CO stretches. Panel (b): power spectra of the four effective modes. Panel (c): power spectra in the set of effective modes extended to represent the overtones. In the middle and bottom panels, the moving frame described in the text has been used, resulting in the elimination of the rotational broadening of the peaks compared to Figure 2.

The power spectrum of the symmetric stretch clearly exhibits the double peak feature characteristic of the Fermi resonance. With a vibrational basis of four internal modes it is then not possible to discriminate the origin of the two peaks. This can instead be done by extending the set of effective modes as indicated at the end of Sections II A and III B. In particular, we add to the set of four modes used in Figure 3(b)the functions $\theta_x(t)\dot{\theta}_x(t)$ and $\theta_y(t)\dot{\theta}_y(t)$. Figure 3(c) shows the power spectra of the new localized modes. Three peaks now appear in the region around 1260 cm⁻¹. The central feature, located at $\omega_{2b} = 1261 \text{ cm}^{-1}$, is close to the double of $\omega_b = 634$ cm⁻¹. This is the power spectrum of the asymmetric combination $\theta_x(t)\dot{\theta}_x(t) - \theta_y(t)\dot{\theta}_y(t)$, which by symmetry cannot couple to the symmetrical stretch, and we thus assign it to a pure bend overtone. The two side peaks at $\omega_{-} = 1233 \text{ cm}^{-1}$ and $\omega_{+} = 1317 \text{ cm}^{-1}$ are now well localized modes with a single peak feature. The mode localization procedure³⁸ attributes them to linear combinations of the symmetric stretch, $r_1 + r_2$, and the symmetric bend overtone $\theta_x(t)\dot{\theta}_x(t) + \theta_y(t)\dot{\theta}_y(t)$. This unambiguously shows that the double peak feature observed in the vibrational density of states indeed arises from a Fermi resonance coupling these two modes.

The weight of each mode in this decomposition can be quantified as described in Sec. III, Eq. (9), and subsequent discussion. We obtain that the lower peak of the Fermi dyad is composed of 36% of the symmetric stretch and of 32% of each bend overtone. Symmetrically, the weight of the symmetric stretch in the higher peak is 66% and that of each bend overtone is 17%. The resonance is not perfect as the weight of the symmetric stretch is not exactly 50%.

The analysis described above was repeated on MD spectra computed at different temperatures to obtain a quantitative estimate of the splitting $\Delta \omega_c = \omega_+ - \omega_-$ as a function of *T*. The splitting at different temperatures is the best quantity to compare with experiments, since the absolute peak position is shifted (as already remarked by Windisch *et al.*³⁵) due to the functional employed. The experimental Raman spectra as a function of temperature in the Fermi dyad region are reported in Figure 4. Note that the experimental peak position for the dyad at 315 K compares well with the previously reported data at 313 K³⁵: 1278 and 1383 cm⁻¹ from the present data vs 1285 and 1389 cm⁻¹ from the one reported by Windsch *et al.*³⁵

Figure 4 shows the experimental spectra obtained for supercritical CO_2 at different temperatures and pressures. Note that the high frequency part of the Fermi dyad has an intensity about twice that of the low frequency part. This is in very good agreement with the mode localization analysis of the simulation results, which assigns a weight twice as large for the symmetric stretch to the higher frequency peak as compared to the lower frequency peak.

Figure 4, however, also shows some striking differences with the DFT-based classical calculations. In particular, in experiments each "shoulder" in the Fermi dyad is in fact a multiplet. As the temperature increases, satellite peaks appear close to the main ones and grow in intensity. As indicated in the seminal Fermi paper,¹ the satellite peaks originate from resonance transitions from different initial vibrational states. The intensity of these peaks is related to the thermal population while their position is fixed by the energy of the quantum



FIG. 4. Experimental Raman spectra of CO₂ in the Fermi dyad region. Black curve: T = 315 K, P = 120 bars; orange curve: T = 550 K, P = 660 bars; red curve: T = 773 K, P = 1160 bars.

levels. These features are absent in the computational spectra of Figure 3, obtained directly from the Newtonian simulations on the DFT potential (with no use of the theory developed in Section II B), by computing the Fourier transform of the fully classical velocity time-auto correlation function. This fully classical correlation function cannot reflect the quantization of vibrational modes or the correct quantum thermal population of these modes. To compare experiments and simulations, we have then focused on the average frequency in the experimental multiplets and in the broad simulations peaks. Averaging alone is, however, not sufficient to capture in the simulation the variation of the relative intensities of the satellite peaks with temperature as reflected in the shift of the position of the center of mass (i.e., first moment) of the multiplets. Table I reports the experimental and DFT-based splitting as a function of temperature. The values of the frequencies used to determine the splitting correspond to the center of mass of the high and low frequency bands in Figures 2 and 4. Both experiments and simulations show a strong dependence of the splitting on temperature. The agreement between calculations and experimental data is good at high temperatures, but at T= 315 K, the classical DFT-based result underestimates the splitting by about 25 cm⁻¹. This finding is a consequence of the near \sqrt{T} dependence of the classical splitting discussed in Section II B and indicates that nuclear quantum effects are already relevant for CO₂ at experimentally relevant conditions. At high temperatures, the results of the simulations with Newtonian dynamics are in better agreement with the experiments because anharmonicities are fully accounted for and a

TABLE I. Experimental Fermi splittings ($\Delta \omega^{Exp}$) and values obtained from the DFT-based molecular dynamics ($\Delta \omega_c^{sim}$). Values are reported in cm⁻¹.

Т (К)	$\Delta \omega^{Exp}$	$\Delta \omega_c^{sim}$
315	109.5	84.4
550	118.6	122.0
773	131.9	133.4

classical approximation for the nuclear properties becomes more appropriate.

In Sec. IV B we show that our perturbative approach can correct for this. This can be rationalized as follows. In quantum mechanics, the position of the center of mass of the peaks is related to the value of a correlation function at short times. For these short times, a classical approximation of the dynamics is sufficient to describe the time evolution of the correlation function, provided that the correct quantum thermal average is sampled. This has been demonstrated by several calculations based on linearized and other approximate methods for computing quantum time correlation functions.^{64–71} In these approximate methods, sampling of the quantum thermal probability is obtained by brute force, but this is too expensive for a range of condensed phase applications. The procedure that we adopt circumvents this problem by including quantum effects in the thermal averages analytically via perturbation theory. The physics described in this way focuses on the initial population of energy levels and average quantum fluctuations of the vibrational modes. Note that our computational approach (including the quantum perturbative treatment) does not allow assigning the experimental multiplets to any specific state-to-state transition, since it is by construction restricted to average properties "smeared" over the multiplets. This level of analysis is beyond the capability of a method still fundamentally based on classical time evolution and on a very simple model Hamiltonian.

As a final comment, note that the experimental spectra also show that the pressure dependence of the features is small, supporting our theoretical development where only temperature is explicitly taken into account. This weak dependence can be rationalized by observing that pressure impacts the vibrational frequencies only via intermolecular interactions, a negligible effect at the considered densities as confirmed by the fact that the frequencies of the bending and the asymmetric stretch in Figure 2 do not change. Further support to this assumption comes from recent work on solid CO₂ under pressure,⁷² showing that appreciable effects on the dyad require pressures order of magnitudes larger than those considered here. Experiments at a fixed temperature^{73,74} also show that appreciable (few wave numbers) effects on the position and width of the bands require huge density variations. The density range spanned in our simulations and experiments is much smaller, and we can then consider the temperature effects dominant. Note, however, that density will affect the interaction between the CO₂ molecules and local formation of clusters⁷⁵ and thus the unperturbed vibrational quantum levels of each CO2 molecule. The extent to which this will also modify the coupling constant is indeed an interesting question for future work. We have assumed here that, in the small density range we have considered, this dependence is negligible. In a different context, the effect of solvents on the Fermi resonance was studied by coupling the simple Fermi model with resonance Raman experiments and ab initio calculations for a carotenoid molecule. In that case, the environment turned out to have a primary effect on the fundamental (unperturbed) frequencies and through it on the resonance splitting, while the effect on the coupling could be ignored.9

B. Quantum perturbation theory applied to CO₂

To account for nuclear quantum effects on the splitting, we now apply the theory developed in Section II B to the case of CO₂. Recall that in this case, the high frequency mode, *x*, is the symmetric stretching, while the two degenerate low frequency modes, ξ and η , are the bendings in *xy* and *yz* planes (we employ the axis convention of Figure 1).

The values of the parameters in the model Hamiltonian, Eq. (11), are specified as follows. The frequencies ω_1 and ω_2 are determined from the effective normal mode procedure described above applied to the classical dynamics of the nuclei (see Figure 3). Once again, we stress that these effective frequencies reflect the anharmonicity of the potential energy surface. For the masses of the modes, we adopt the standard reduced masses of CO₂.⁷⁶ χ_{12} is estimated from the classical MD by inverting Eq. (31). We obtained three values for χ_{12} using the classical splittings reported in Table I at the three simulated temperatures and used their average as our best estimate. We observe very small variations of χ_{12} at the three temperatures, within 3% of the average value, justifying our model with χ_{12} assumed independent of temperature.

We then correct for quantum effects by solving the generalized eigenvalue problem, Eq. (14), with the value of the coupling computed as described above and using the effective frequencies obtained from the localization procedure as the average frequency for each band. The resulting Fermi splitting of CO_2 as a function of temperature is shown in Figure 5 and compared with experiments and the classical model. In the figure, the experimental splittings are shown as triangles, while the solid curve reports the result of the quantum perturbative approach with the values of the model obtained from the DFT-based simulations as described above, and the classical model results are shown as a dotted-dashed curve. At



FIG. 5. Splitting of the Fermi dyad in supercritical CO_2 as a function of temperature obtained via: experiments (triangles); DFT-MD (crosses); quantum model with coupling and frequencies from DFT-MD (solid curve); quantum model with coupling and frequencies from the experiment (dashed curve); classical model (dotted-dashed curve).

T = 315 K, the agreement with experiments is nearly perfect demonstrating the effectiveness of the quantum correction. This is even more striking when comparing with the result from the bare DFT-MD simulation, shown as crosses. The accuracy of the quantum correction at low temperatures can be further appreciated by considering the $T \rightarrow 0$ limit. The incorrectness of the classical model shown in the same figure suggests that a classical dynamics approach should fail in reproducing the quantum splitting from about 500 K down to 0 K. The experimental behavior can be extrapolated from Figure 4 by observing that the intensity of the satellite peaks goes to zero with the temperature. The separation of the maxima of the two main experimental peaks then provides us with an estimate of the splitting at T = 0 K. This splitting is $\Delta \omega^*(\exp) = 104$ cm⁻¹. The splitting at T = 0 K calculated from the analytical quantum expression (see Eq. (35)) is $\Delta \omega^*$ (th.) = 104.1 ± 3cm⁻¹, in excellent agreement with the experimental value (the error of 3 cm^{-1} is estimated from the uncertainty on the average value of χ_{12} from our three estimates).

Figure 5 shows that the agreement between the prediction of the analytical quantum approach and experiments deteriorates slightly at higher temperatures with errors of 8 cm⁻¹ and 12 cm^{-1} at T = 550 K and T = 773 K, respectively. We attribute this to the deficiencies of the density functional used for the DFT-MD simulation. To verify this hypothesis, we have also derived parameters for the quantum model (ω_1 , ω_2 , and χ_{12}) directly from experiments. The dashed curve in Figure 5 shows the temperature dependence of the splitting as obtained by parameters extracted from experiments. The agreement with experimental values is now very good in the whole temperature range, showing that the perturbative treatment and the simple Fermi Hamiltonian model lead to quantitative predictions even at high temperatures. The frequencies extracted from the experimental spectra are about 5% higher than those obtained from DFT-MD, typical for density functional calculations at the level adopted here.

A satisfactory agreement is also reached for the coupling parameter for which the DFT-MD based value is 5% higher than the one based on the experiment. This slightly larger value compensates for the lack of quantum effects at high temperatures in Newtonian simulations, see Figure 5. At room temperature and below, however, classical DFT-MD qualitatively fails to reproduce the behavior of the Fermi splitting.

V. CONCLUSIONS

DFT-based classical simulations were combined with analytical results obtained via quantum perturbation theory to study the Fermi resonances. The approach described makes it possible to study non-linear resonances including quantum nuclear effects in realistic condensed phase simulations with affordable numerical effort and was used to investigate more in detail peak assignment and the behavior of the Fermi dyad splitting with temperature in the paradigmatic case of supercritical CO_2 .

We first showed how the dyadic feature in the calculated spectrum can be unambiguously assigned to a Fermi resonance via a mode localization procedure that identifies appropriate combinations of internal vibrational modes of the molecule.

The mode localization procedure, originally devised for classical vibrations, was here generalized to the quantum case and extended (both classically and quantum) to include overtones. Furthermore, by adopting the model Hamiltonian proposed by Fermi, the problem of identifying the Fermi modes and the splitting as a function of temperature was analytically solved via a perturbative treatment in the coupling parameter γ_{12} . With this approach, we are able to characterize correctly the behavior of the splitting, defined as the difference between the first moments of the multiplets in the experimental Fermi dyad, as a function of temperature, with increasing accuracy at low temperatures where the effective model Hamiltonian becomes a better model for the system. It was also shown that the coupling parameter, the only unknown in our model, can be obtained from the DFT-based classical calculations or experiments.

Comparison with experiments shows that the protocol introduced in this work reproduces the correct behavior of the splitting in the zero temperature limit and gives results that are in very good agreement with experiments over a significant range of temperatures for the prototypical case of supercritical CO₂. Within the limits discussed in Sec. II, the two steps proposed to identify the resonance and include quantum effects are however applicable to general systems. Note in particular that, in discussing our quantum correction procedure, we distinguished the role of quantum effects on the dynamics and on the sampling of initial conditions. Our procedure approximately accounts for quantum thermal effects, which include both zero point energy and the population of higher vibrational states at a finite temperature. When quantum effects are important in the dynamics, the method proposed for correcting the spectra will likely fail. An example of this kind is, probably, the Fermi resonance in the Zundel cation, as exemplified by the difficulty for path-integral techniques to reproduce the correct spectra although there is correct sampling of the quantum distribution.⁷⁷ Even in these situations, however, the first analysis tool described in this work, i.e., the mode localization procedure, can be used to interpret and assign Fermi dyads. Note also that this procedure could also be used in conjunction with other approximate methods for the dynamic, such as ring-polymer, centroid, linearized, or even semiclassical approaches, since it operates only on the basis of correlation functions. Finally, note also that the procedure was applied in this work to a 1:2 resonance, but it can be generalized to any vibrational level and combination band resonances. Future work will focus on these developments.

SUPPLEMENTARY MATERIAL

See supplementary material for Mathematica notebook for the perturbative calculation of Fermi splitting at a finite temperature for the case of CO_2 . We supply a pdf file as well as a file which can be loaded directly into Mathematica.

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