

Spontaneous symmetry breaking and inversion-line spectroscopy in gas mixtures

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According to quantum mechanics, chiral molecules, that is, molecules that rotate the polarization of light, should not exist. The simplest molecules which can be chiral have four or more atoms with two arrangements of minimal potential energy that are equivalent up to a parity operation. Chiral molecules correspond to states localized in one potential energy minimum and can not be stationary states of the Schrödinger equation. A possible solution of the paradox can be founded on the idea of spontaneous symmetry breaking. This idea was behind work we did previously involving a localization phase transition: at low pressure, the molecules are delocalized between the two minima of the potential energy while at higher pressure they become localized in one minimum due to the intermolecular dipole-dipole interactions. Evidence for such a transition is provided by measurements of the inversion spectrum of ammonia and deuterated ammonia at different pressures. A previously proposed model gives a satisfactory account of the empirical results without free parameters. In this paper, we extend this model to gas mixtures. We find that also in these systems a phase transition takes place at a critical pressure which depends on the composition of the mixture. Moreover, we derive formulas giving the dependence of the inversion frequencies on the pressure. These predictions are susceptible to experimental test.

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I. INTRODUCTION

The existence of chiral molecules, that is, molecules that rotate the polarization of light, has so far no universally accepted explanation. Hund was the first to point out in 1927 that such molecules according to quantum mechanics should not exist as the corresponding Hamiltonian is invariant under mirror reflection [1]. This problem became known as Hund's paradox and was discussed in the physicochemical literature for decades. A possible solution of the paradox can be founded on the idea of spontaneous symmetry breaking (SSB) once we take into account that the experiments deal with a large number of molecules and that their interactions are sufficient to keep them in the chiral state. This idea was behind work done previously [2–8] where the explanation of the existence was based on a localization phenomenon.

Pyramidal molecules, i.e., molecules of the kind XY_3 such as ammonia NH_3 , phosphine PH_3 , arsine AsH_3 , are potentially chiral. Suppose that we replace two of the hydrogens with different atoms such as deuterium and tritium: we obtain a molecule of the form $XYWZ$. This is called an enantiomer, that is, a molecule whose mirror image can not be superimposed to the original one. These molecules are optically active in states where the atom X is localized on one side of the YZ plane. In the following, we shall refer to potentially chiral molecules such as ammonia as prechiral molecules. Another example of prechiral molecule, not pyramidal, is deuterated disulfane D_2S_2 (see Fig. 1).

According to quantum mechanics, chiral molecules should not exist as stable stationary states. Consider a pyramidal molecule XY_3 . The two possible positions of the X atom with respect to the plane of the Y atoms are separated by a potential barrier and can be connected via tunneling. This gives rise to stationary wave functions delocalized over the two minima of the potential and of definite parity. In particular, the ground state is expected to be even under parity. Tunneling induces a doublet structure of the energy levels.

On the other hand, the existence of chiral molecules can be interpreted as a phase transition. In fact, isolated molecules do not exist in nature and the effect of the environing molecules must be taken into account. This interpretation underlies a simple mean-field model that we have developed [7] to describe the transition of a gas of NH_3 molecules from a nonpolar phase to a polar one through a localization phenomenon which gives rise to the appearance of an electric dipole moment. Even if ammonia molecules are only prechiral, the mechanism, as emphasized in [7], provides the key to understand the origin of chirality.

A quantitative discussion of the collective effects induced by coupling a molecule to the environment constituted by the other molecules of the gas was made in [3]. In this work, it was shown that, due to the instability of tunneling under weak perturbations, the order of magnitude of the molecular dipole-dipole interaction may account for localized ground states. This suggested that a transition to localized states should happen when the interaction among the molecules is increased.

Evidence for such a transition was provided by measurements of the dependence of the doublet frequency under increasing pressure: the frequency vanishes for a critical pressure P_{cr} different for NH_3 and ND_3 . The measurements were taken at the end of the 1940s and beginning of the 1950s [9–11] but no quantitative theoretical explanation was given for 50 years. Our model [7] gives a satisfactory account of the empirical results. A remarkable feature of the model is that there are no free parameters. In particular, it describes quantitatively the shift to zero frequency of the inversion line of NH_3 and ND_3 on increasing the pressure.

In this paper, we extend our model to gas mixtures. This case may be of interest, among other things, for the interpretation of the astronomical data like those from Galileo spacecraft [12] which measured the absorption spectrum of NH_3 in the Jovian atmosphere.

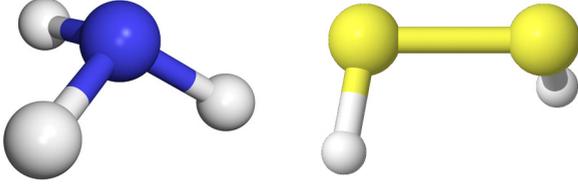


FIG. 1. (Color online) Molecular structures of ammonia (NH_3 , left) and deuterated disulfane (D_2S_2 , right) in one of their two localized states.

The main results of this work are as follows.

(i) Also in the case of mixtures there is a quantum phase transition between a delocalized (or achiral, or nonpolar) phase and a localized (or chiral, or polar) phase. At fixed temperature, the crossover between the two phases is determined by a properly defined critical pressure P_{cr} .

(ii) We derive formulas expressing the critical pressure of the mixture in terms of the doublet splittings of the isolated chiral molecules and the fractions of the constituents. For a binary mixture with fractions x_1 and x_2 of the two species, we have

$$\frac{1}{P_{\text{cr}}} = \sum_{i=1}^2 x_i \frac{1}{P_{\text{cr}}^{(i)}}.$$

Supposing that species 1 is chiral, $P_{\text{cr}}^{(1)}$ is the critical pressure of the pure unmixed species, namely, $P_{\text{cr}}^{(1)} = \Delta E_1 / (2\gamma_{11})$, with ΔE_1 being the rarefied-gas doublet splitting and γ_{11} given in terms of the temperature and other microscopic parameters, i.e., the electric dipole moment and the collision diameter of molecules 1 [see Eq. (24)]. If species 2 is nonpolar, then $P_{\text{cr}}^{(2)} = \Delta E_1 / (2\gamma_{12})$ with γ_{12} expressing the polarization of molecules of species 2 by the chiral molecules of species 1 [see Eq. (10)]. If species 2 is chiral, then $P_{\text{cr}}^{(2)} = \Delta E_2 / (2\gamma_{22})$ with γ_{22} expressing the self-consistent interaction among the molecules of species 2 [see Eq. (24)]. In both cases, the inverse critical pressure of the mixture is the fraction-weighted average of the inverse critical pressures of its components. The result is easily generalized to mixtures made up of an arbitrary number of components.

(iii) We derive formulas giving the dependence of the inversion frequencies on the pressure [see Eqs. (12) and Sec. VB]. These results are susceptible to experimental test.

The paper is structured as follows. In the next section, we briefly recall the mean-field model for a single gas of molecules exhibiting inversion doubling like ammonia. In particular, we discuss the interaction mechanism and the strength of the interaction leading to a localization quantum phase transition with the disappearance of the inversion line. In Sec. III, we describe the well-known reaction field mechanism which provides exactly the same interaction strength. The reason for arguing in terms of the reaction field is its simplicity especially in view of its extension to gas mixtures. In Sec. IV, we consider mixtures of a chiral gas with nonpolar molecules, such as, for instance, $\text{NH}_3\text{-H}_2\text{-He}$. In Sec. V, we consider mixtures of chiral gases. For convenience of the reader, we have added three appendixes. They give details on the model [7] and the comparison with the experiments [9–11].

II. CHIRAL MOLECULES AS A CASE OF SPONTANEOUS SYMMETRY BREAKING

We model a gas of prechiral, e.g., pyramidal, molecules as a set of two-level quantum systems, that mimic the inversion degree of freedom of an isolated molecule, mutually interacting via the dipole-dipole electric force.

The Hamiltonian for the single isolated molecule is assumed of the form $-\sigma^x \Delta E / 2$, where ΔE is the inversion energy splitting measured in a rarefied gas of the considered species and

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

is the Pauli matrix with symmetric and antisymmetric delocalized tunneling eigenstates φ_+ and φ_- :

$$\varphi_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \varphi_- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

Since the rotational degrees of freedom of an isolated molecule are faster than the inversion ones, on the time scales of the inversion dynamics, namely $\hbar / \Delta E$, the molecules in a gas feel an attraction arising from the angle averaging of the effective dipole-dipole interaction at the actual temperature of the gas [13]. The localizing effect of the dipole-dipole interaction between two molecules i and j can be represented by an interaction term of the form $-\mathfrak{g}_{ij} \sigma_i^z \otimes \sigma_j^z$, with $\mathfrak{g}_{ij} > 0$, where

$$\sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

is the Pauli matrix with left and right localized eigenstates φ_L and φ_R :

$$\varphi_L = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \varphi_R = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The Hamiltonian for N interacting molecules then reads as

$$H = -\frac{\Delta E}{2} \sum_{i=1}^N \sigma_i^x - \sum_{i=1}^N \sum_{j=i+1}^N \mathfrak{g}_{ij} \sigma_i^z \otimes \sigma_j^z. \quad (1)$$

For a gas of moderate density, we approximate the behavior of the $N \gg 1$ molecules with the mean-field Hamiltonian

$$h(\psi) = -\frac{\Delta E}{2} \sigma^x - \frac{G}{N} \langle \psi, \sigma^z \psi \rangle \sigma^z, \quad (2)$$

where ψ is the mean-field molecular state to be determined self-consistently by solving the nonlinear eigenvalue problem associated with Eq. (2) and the normalization condition $\langle \psi, \psi \rangle = N$. The scalar product between two Pauli spinors ψ and ϕ is defined in terms of their two components in the standard way:

$$\langle \psi, \phi \rangle = \bar{\psi}_1 \phi_1 + \bar{\psi}_2 \phi_2.$$

The parameter G accounts for the effective dipole interaction energy of a single molecule with the rest of the gas. It must be identified with a sum over all possible molecular distances and all possible dipole orientations calculated assuming that, concerning the translational, vibrational, and rotational degrees of freedom, the N molecules behave as an ideal gas at thermal equilibrium at temperature T . This assumption relies

on a sharp separation (decoupling) between these degrees of freedom and the inversion motion [14].

We now discuss the calculation of G following Keesom [13]. An alternative derivation of G will be shown later based on the so-called reaction field mechanism.

Let us define an effective interaction potential $V(r)$ between two electric dipoles at distance r via the formula

$$e^{-V(r)/k_B T} = \langle e^{-V(r, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2)/k_B T} \rangle,$$

where

$$V(r, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2) = \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\mathbf{r} \cdot \boldsymbol{\mu}_2)r^{-2}}{4\pi\epsilon_0 r^3}$$

is the standard dipole-dipole interaction potential and $\langle \dots \rangle$ denotes the average over all possible orientations of the vectors $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$. Assuming that $V(r) \ll k_B T$ and observing that $\langle V(r, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2) \rangle = 0$, we approximately evaluate the effective potential as

$$\begin{aligned} V(r) &= -\frac{1}{2} \left\langle \left(\frac{V(r, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2)}{k_B T} \right)^2 \right\rangle k_B T \\ &= -\frac{\mu_1^2 \mu_2^2}{3(4\pi\epsilon_0)^2 k_B T r^6}. \end{aligned}$$

In the case of a gas of molecules with dipole moments μ , the effective interaction energy of one molecule with the rest of the gas amounts to $-G$, where

$$\begin{aligned} G &= \int_d^\infty \rho(r) \frac{\mu^4}{3(4\pi\epsilon_0)^2 k_B T r^6} 4\pi r^2 dr \\ &= \frac{4\pi}{9} \frac{\mu^4 P}{(4\pi\epsilon_0 k_B T)^2 d^3}. \end{aligned} \quad (3)$$

To get the above result, we used $\rho(r) = P/k_B T$, the ideal gas density at pressure P and temperature T . Note that d is the minimal distance at which two molecules can be found, namely, the so-called molecular collision diameter. At fixed temperature, the effective interaction constant G increases linearly with the gas pressure P .

The nonlinear eigenvalue problem associated with Eq. (2) is solved in detail in Appendix A. There exists a critical value of the interaction strength $G_{\text{cr}} = \Delta E/2$, such that for $G < G_{\text{cr}}$ the mean-field eigenstate with minimal energy is $\psi = \sqrt{N}\varphi_+$, with delocalized molecules, whereas for $G > G_{\text{cr}}$ there are two degenerate states of minimal energy. These are chiral states transformed into each other by the parity operator σ^x approaching the localized states φ_L, φ_R for $G \gg G_{\text{cr}}$. We thus have a quantum phase transition between a delocalized (or achiral, or nonpolar) phase and a localized (or chiral, or polar) phase. In view of the dependence of G on P , we can define a critical pressure at which the phase transition takes place:

$$P_{\text{cr}} = \frac{9}{8\pi} \frac{\Delta E d^3 (4\pi\epsilon_0 k_B T)^2}{\mu^4}. \quad (4)$$

In Table I, we report the values of P_{cr} calculated for different prechiral molecules.

In Appendix B, we show that in the delocalized phase the inversion angular frequency of the interacting molecules

TABLE I. Rarefied-gas energy splitting ΔE , electric dipole moment μ , and collision diameter d measured for different prechiral molecules [14,15]. In the fourth column, we report the critical pressure P_{cr} evaluated by Eq. (4) at $T = 300$ K.

	ΔE (cm ⁻¹)	μ (Debye)	d (Å)	P_{cr} (atm)
NH ₃	0.81	1.47	4.32	1.69
ND ₃	0.053	1.47	4.32	0.11
D ₂ S ₂	10 ⁻⁹	1.56	5.97	4.3 × 10 ⁻⁹

depends on the pressure as

$$\hbar\bar{\omega} = \Delta E \sqrt{1 - \frac{P}{P_{\text{cr}}}}. \quad (5)$$

This formula is interesting as it expresses the ratio of two microscopic quantities $\hbar\bar{\omega}$ and ΔE as a universal function of the ratio of the macroscopic variables P and P_{cr} . Furthermore, it provides a very good representation of some spectroscopic data, namely, the shift to zero frequency of the inversion line of NH₃ or ND₃, as it appears from Fig. 11 (see Appendix C for more details).

III. REACTION FIELD MECHANISM

The mean-field coupling constant G introduced in Sec. II can be estimated, obtaining the same result, using a different argument which can be easily generalized. This is the reaction field mechanism widely used in physics and chemistry [16,17].

Let us consider a spherical cavity of radius a in a homogeneous dielectric medium characterized by a relative dielectric constant ϵ_r . An electric dipole $\boldsymbol{\mu}$ placed at the center of the cavity polarizes the dielectric medium inducing inside the sphere a reaction field \mathbf{R} proportional to $\boldsymbol{\mu}$:

$$\mathbf{R} = \frac{2(\epsilon_r - 1)}{2\epsilon_r + 1} \frac{\boldsymbol{\mu}}{4\pi\epsilon_0 a^3}.$$

As a result, the dipole acquires an energy

$$\mathcal{E} = -\frac{1}{2} \boldsymbol{\mu} \cdot \mathbf{R} = -\frac{\epsilon_r - 1}{2\epsilon_r + 1} \frac{\mu^2}{4\pi\epsilon_0 a^3}. \quad (6)$$

By using the Clausius-Mossotti relation

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3} \rho(\alpha + \alpha^{\text{D}}),$$

where α is the molecular polarizability and $\alpha^{\text{D}} = \mu^2/(3\epsilon_0 k_B T)$ is the Debye (orientation) polarizability, and observing that for a chiral gas $\alpha^{\text{D}} \gg \alpha$ (for instance, in the case of NH₃ we have $\alpha \simeq 2 \text{Å}^3$ whereas $\alpha^{\text{D}} \simeq 217 \text{Å}^3$ at $T = 300$ K), we get

$$\mathcal{E} = -\frac{4\pi}{9} \frac{\mu^4 P}{(4\pi\epsilon_0 k_B T)^2 a^3}.$$

In all the above expressions we have $\epsilon_r \simeq 1$ so that we approximated $\epsilon_r + 2 \simeq 2\epsilon_r + 1 \simeq 3$.

We exactly have $\mathcal{E} = -G$ provided $a = d$, where d is the molecular collision diameter introduced in Eq. (3) as the minimum distance between two interacting molecules. In fact, the size of the spherical cavity is not arbitrary. Microscopic

arguments [18,19] show that a must be identified with the radius of an effective hard core, namely, the molecular collision diameter d .

IV. MIXTURES OF A CHIRAL GAS WITH NONPOLAR MOLECULES

By using the reaction field approach to the coupling constant G , we now generalize the mean-field model of Sec. II to the case of a mixture of chiral with nonpolar molecules. Consider a gas mixture of two species labeled 1 and 2. In this case, the Clausius-Mossotti relation reads as

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{1}{3} [\rho_1 (\alpha_1 + \alpha_1^D) + \rho_2 (\alpha_2 + \alpha_2^D)].$$

If species 1 is prechiral, i.e., polar, α_1 can be neglected with respect to α_1^D and if species 2 is nonpolar, $\alpha_2^D = 0$. The energy acquired by one molecule of the polar species, having electric dipole moment μ_1 , then is

$$\mathcal{E}_1 = -\frac{1}{3} \rho_1 \alpha_1^D \frac{\mu_1^2}{4\pi \varepsilon_0 d_{11}^3} - \frac{1}{3} \rho_2 \alpha_2 \frac{\mu_1^2}{4\pi \varepsilon_0 d_{12}^3}, \quad (7)$$

where d_{11} and d_{12} are the diameters of the molecular collisions 1-1 and 1-2, namely, $d_{11} = 2r_1$ and $d_{12} = r_1 + r_2$, r_1 and r_2 being the hard-sphere radii of the molecules 1 and 2. If the density ρ_1 is such that $\rho_1 \alpha_1^D \ll \rho_2 \alpha_2$, the above formula reduces to

$$\mathcal{E}_1 = -\frac{1}{3} \rho_2 \alpha_2 \frac{\mu_1^2}{4\pi \varepsilon_0 d_{12}^3}.$$

This formula approximates the case of a single polar molecule immersed in a nonpolar gas.

For a mixture of chiral and nonpolar molecules, the mean-field molecular state of the chiral species 1, ψ_1 , is determined similarly to the case of a single chiral gas. The only degree of freedom of the nonpolar molecules is the deformation which, in turn, is proportional to the electric dipole moment of the chiral molecules. Therefore, we assume the following nonlinear Hamiltonian similar to Eq. (2):

$$h_1(\psi_1) = -\frac{\Delta E_1}{2} \sigma_1^x - \frac{G_1}{N_1} \langle \psi_1, \sigma_1^z \psi_1 \rangle \sigma_1^z. \quad (8)$$

The mean-field molecular state ψ_1 is normalized to the number of molecules of the species 1, namely $\langle \psi_1, \psi_1 \rangle = N_1$. The parameter G_1 accounts for the effective dipole interaction energy of a single chiral molecule with the rest of the gas constituted by polar and nonpolar species. According to the reaction field arguments, we have just to identify $G_1 = -\mathcal{E}_1$, where \mathcal{E}_1 is given by Eq. (7). Thus, we see that G_1 is the sum of two contributions

$$G_1 = G_{11} + G_{12},$$

where

$$G_{11} = \frac{4\pi}{9} \frac{\mu_1^4 P_1}{(4\pi \varepsilon_0 k_B T)^2 d_{11}^3} = \gamma_{11} P_1 \quad (9)$$

is the energy provided by the interaction with the chiral species and

$$G_{12} = \frac{1}{3} \frac{\alpha_2 \mu_1^2 P_2}{4\pi \varepsilon_0 k_B T d_{12}^3} = \gamma_{12} P_2 \quad (10)$$

the energy due to the presence of the nonpolar molecules. In the above expressions, we used the ideal gas relations $\rho_1 = P_1/k_B T$ and $\rho_2 = P_2/k_B T$, P_1 and P_2 being the partial pressures of the species 1 and 2.

The analysis of the mean-field Hamiltonian (8) is identical to the case of a single chiral gas. We have a localization phase transition when G_1 becomes equal to $G_{1cr} = \Delta E_1/2$. The transition can be considered as a function of the total pressure $P = P_1 + P_2$ of the mixture and of the fractions of the two species $x_1 = P_1/P$ and $x_2 = P_2/P$. In this case, an important prediction is that, instead of a unique critical pressure, we have a critical line parametrized by x_1 (or $x_2 = 1 - x_1$):

$$P_{cr}(x_1) = \frac{\Delta E_1}{2x_1\gamma_{11} + 2(1-x_1)\gamma_{12}}, \quad (11)$$

where $\gamma_{11} = G_{11}/P_1$ and $\gamma_{12} = G_{12}/P_2$ with G_{11} and G_{12} as in Eqs. (9) and (10).

The inversion frequency of the chiral species 1 can be evaluated as in the case of a single chiral gas. The result is formally identical to that in Eq. (5),

$$\hbar\bar{\omega}_1 = \Delta E_1 \sqrt{1 - \frac{P}{P_{cr}(x_1)}}, \quad (12)$$

with the angular frequency $\bar{\omega}_1$ which is now a function of the pressure P of the mixture and of the fraction x_1 of the chiral species. However, for any fixed value of x_1 , the ratio $\hbar\bar{\omega}_1/\Delta E_1$ is still a universal function of P/P_{cr} independent of the nature of species 1.

In Fig. 2, we show the variation of the critical pressure as a function of the fraction x of the chiral species for the mixtures $\text{NH}_3\text{-He}$ and $\text{D}_2\text{S}_2\text{-He}$. The value of P_{cr} at $x = 1$ coincides with that reported in Table I for a pure chiral gas, whereas for $x \rightarrow 0$ the critical pressure approaches a much higher value. The ratio

$$\frac{\lim_{x \rightarrow 0} P_{cr}(x)}{P_{cr}(1)} = \frac{4\pi}{3} \frac{\mu_1^2 / (4\pi \varepsilon_0 d_{11}^3)}{k_B T} \frac{d_{12}^3}{\alpha_2}$$

amounts to about 400 in the examples of Fig. 2.

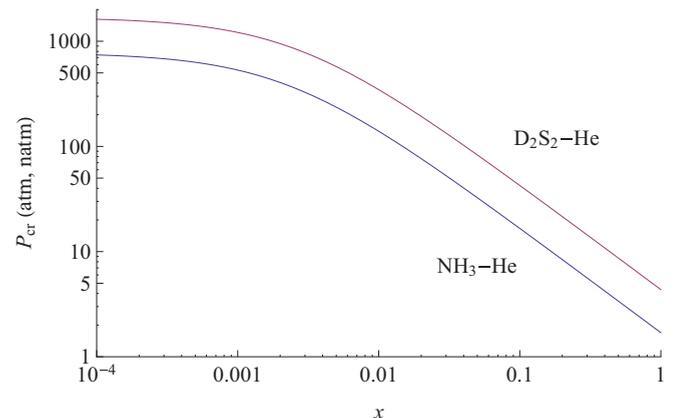


FIG. 2. (Color online) Critical pressure P_{cr} as a function of the chiral species fraction x for $\text{NH}_3\text{-He}$ (bottom) and $\text{D}_2\text{S}_2\text{-He}$ (top) mixtures at $T = 300$ K. Note that pressure units are atm in the case of $\text{NH}_3\text{-He}$ and natm in the case of $\text{D}_2\text{S}_2\text{-He}$.

The above analysis is immediately generalized to a mixture containing one chiral gas and an arbitrary number of nonpolar gases. As an example, for a ternary mixture (as before, species 1 is the chiral one) we have a surface of critical pressures

$$P_{\text{cr}}(x_1, x_2) = \frac{\Delta E_1}{2x_1\gamma_{11} + 2x_2\gamma_{12} + 2(1 - x_1 - x_2)\gamma_{13}},$$

where $\gamma_{13} = G_{13}/P_3$ with G_{13} given by an expression analogous to Eq. (10). This term expresses the polarization of the molecules of species 3 by the chiral molecules of species 1.

The above results may be of interest, among other things, in the interpretation of astronomical data like those from Galileo spacecraft [12] which measured the absorption spectrum of NH_3 in the Jovian atmosphere. Note that, since the atmosphere of Jupiter is mostly made of molecular hydrogen and helium in roughly solar proportions whereas ammonia has a tiny fraction, the critical pressure of the mixture is drastically different if compared with the 1.69 atm value of ammonia. For fractions $x_{\text{NH}_3} \simeq 0.01$, $x_{\text{H}_2} \simeq 0.86$, and $x_{\text{He}} \simeq 0.13$, we estimate P_{cr} ranging from 15 atm at $T = 100$ K to 165 atm at $T = 400$ K. This implies that no ammonia inversion-line shift can be observed in microwave absorption measurements performed in the atmosphere of Jupiter.

V. MIXTURES OF CHIRAL GASES

It is possible to extend our mean-field approach to gas mixtures made of several chiral species. We start considering the simplest case of two species.

In Sec. VA, we illustrate the model and evaluate the stationary molecular states of the mixture. In a first reading, one can skip the discussion after Eq. (18) and look at the results summarized in Table II. As in the case of a single chiral gas, the mixture undergoes a localization phase transition at a critical pressure P_{cr} . For $0 < P < P_{\text{cr}}$, the lowest-energy molecular state of the mixture, named d_{++} , corresponds to molecules of both species in a delocalized symmetric configuration. For $P > P_{\text{cr}}$, new minimal-energy molecular states appear with twofold degeneracy. These states, named

TABLE II. Stationary molecular states for a mixture of two chiral gases with fractions $x_1 = N_1/N$ and $x_2 = N_2/N$, $N = N_1 + N_2$ being the total number of molecules. The states are classified in column 1 as delocalized (d) even (+) or odd (−) and chiral (c) left (L) or right (R). This classification results from the decomposition of the two-species molecular states in terms of the delocalized eigenfunctions of σ^x via the coefficients a_1, b_1, a_2, b_2 as in Eq. (18). The values of a_1, b_1, a_2, b_2 are found by solving Eq. (19) with the normalization conditions $a_1^2 + b_1^2 = N_1$ and $a_2^2 + b_2^2 = N_2$. The chiral solutions exist only for $P > P_{\text{cr}}$ and are defined in terms of two parameters q_1 and q_2 shown in Fig. 4. The energy per unit molecule associated with each state [see Eq. (16)] is reported in the last column. For $P < P_{\text{cr}}$ the solution of minimal energy is d_{++} , while for $P > P_{\text{cr}}$ there are two degenerate solutions of minimal energy, namely, c_{LL} and c_{RR} . Other higher-energy states bifurcating at pressures larger than P_{cr} (see Fig. 3) are not reported in this table.

	a_1	b_1	a_2	b_2	\mathcal{E}/N
d_{++}	$\sqrt{N_1}$	0	$\sqrt{N_2}$	0	$-\frac{x_1 \Delta E_1}{2} - \frac{x_2 \Delta E_2}{2}$
d_{+-}	$\sqrt{N_1}$	0	0	$\sqrt{N_2}$	$-\frac{x_1 \Delta E_1}{2} + \frac{x_2 \Delta E_2}{2}$
d_{-+}	0	$\sqrt{N_1}$	$\sqrt{N_2}$	0	$+\frac{x_1 \Delta E_1}{2} - \frac{x_2 \Delta E_2}{2}$
d_{--}	0	$\sqrt{N_1}$	0	$\sqrt{N_2}$	$+\frac{x_1 \Delta E_1}{2} + \frac{x_2 \Delta E_2}{2}$
c_{LL}	$\sqrt{\frac{N_1}{2}(1+q_1)}$	$\sqrt{\frac{N_1}{2}(1-q_1)}$	$\sqrt{\frac{N_2}{2}(1+q_2)}$	$\sqrt{\frac{N_2}{2}(1-q_2)}$	$-\sum_i \frac{x_i q_i \Delta E_i}{2} - \sum_{i,j} \frac{x_i x_j \sqrt{1-q_i^2} \sqrt{1-q_j^2} \gamma_{ij} P}{2}$
c_{RR}	$\sqrt{\frac{N_1}{2}(1+q_1)}$	$-\sqrt{\frac{N_1}{2}(1-q_1)}$	$\sqrt{\frac{N_2}{2}(1+q_2)}$	$-\sqrt{\frac{N_2}{2}(1-q_2)}$	$-\sum_i \frac{x_i q_i \Delta E_i}{2} - \sum_{i,j} \frac{x_i x_j \sqrt{1-q_i^2} \sqrt{1-q_j^2} \gamma_{ij} P}{2}$

c_{LL} and c_{RR} , correspond to molecules of both species in a chiral configuration of type L or R . Equation (25) provides a simple formula for P_{cr} . The inverse critical pressure of the mixture is the fraction-weighted average of the inverse critical pressures of its components.

In Sec. VB, we evaluate the excitation energies of a two-species mixture by using the linear-response theory. The results are summarized by Eq. (36). We have two normal modes which at low pressure reduce to the inversion of the component species. By increasing the pressure, the energy of both modes decreases, the smaller one vanishing at $P = P_{\text{cr}}$, the larger one approaching for $P \gg P_{\text{cr}}$ the asymptotic value given by Eq. (37). An example of this behavior is shown in Figs. 5 and 6 in the case of a NH_3 - ND_3 mixture.

Finally, in Sec. VC, we discuss the consistency of the developed theory by considering the absorption coefficient and two limits in which it must reduce to that of a single chiral gas, namely, the limit of zero fraction of one species and the limit of equal species. We also discuss the possibility of experimental tests for the considered NH_3 - ND_3 mixture.

All the above results can be generalized to mixtures of several chiral gases.

A. Molecular states

For a mixture of two chiral gases, the Clausius-Mossotti relation reads as

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3} (\rho_1 \alpha_1^{\text{D}} + \rho_2 \alpha_2^{\text{D}}),$$

where the Debye polarizations $\alpha_i^{\text{D}} = \mu_i^2 / (3\epsilon_0 k_B T)$, $i = 1, 2$, are given in terms of the molecular electric-dipole moments μ_1 and μ_2 of the two species. According to Eq. (6), due to mutual interactions the molecules of species 1 and 2 acquire the energies

$$\begin{aligned} \mathcal{E}_1 &= -\frac{4\pi}{9} \frac{\mu_1^2 \mu_1^2 P x_1}{(4\pi \epsilon_0 k_B T)^2 d_{11}^3} - \frac{4\pi}{9} \frac{\mu_1^2 \mu_2^2 P x_2}{(4\pi \epsilon_0 k_B T)^2 d_{11}^3}, \\ \mathcal{E}_2 &= -\frac{4\pi}{9} \frac{\mu_2^2 \mu_2^2 P x_2}{(4\pi \epsilon_0 k_B T)^2 d_{22}^3} - \frac{4\pi}{9} \frac{\mu_2^2 \mu_1^2 P x_1}{(4\pi \epsilon_0 k_B T)^2 d_{22}^3}. \end{aligned}$$

As usual, we used the ideal gas relations $\rho_i = P_i/k_B T$, $i = 1, 2$, and introduced the fractions $x_1 = P_1/P$ and $x_2 = P_2/P$, where P is the total pressure of the mixture.

We describe the inversion degrees of freedom of the two species by mean-field molecular states ψ_1, ψ_2 normalized to the number of molecules of the corresponding species $\langle \psi_1, \psi_1 \rangle = N_1$, $\langle \psi_2, \psi_2 \rangle = N_2$. Here, ψ_1 and ψ_2 are Pauli spinors and the scalar product is defined as in Sec. II. By writing $\mathcal{E}_i = -\sum_{j=1}^2 G_{i,j}$, $i = 1, 2$, where

$$G_{ij} = \frac{4\pi}{9} \frac{\mu_i^2 \mu_j^2 P x_j}{(4\pi \epsilon_0 k_B T)^2 d_{ii}^3}, \quad (13)$$

and reasoning as in Sec. II, we introduce the following set of two nonlinear Hamiltonians:

$$h_1(\psi_1, \psi_2) = -\frac{\Delta E_1}{2} \sigma_1^x - \sum_{j=1}^2 \frac{G_{1j}}{N_j} \langle \psi_j, \sigma_j^z \psi_j \rangle \sigma_1^z, \quad (14a)$$

$$h_2(\psi_1, \psi_2) = -\frac{\Delta E_2}{2} \sigma_2^x - \sum_{j=1}^2 \frac{G_{2j}}{N_j} \langle \psi_j, \sigma_j^z \psi_j \rangle \sigma_2^z. \quad (14b)$$

Pauli operators now have a label $i = 1, 2$ relative to the species they refer to. Stationary states are obtained by solving the eigenvalue problem

$$h_1(\psi_1, \psi_2) \psi_1 = \lambda_1 \psi_1, \quad (15a)$$

$$h_2(\psi_1, \psi_2) \psi_2 = \lambda_2 \psi_2, \quad (15b)$$

where λ_1, λ_2 are the Lagrange multipliers associated with the conservation of the particle number of species 1 and 2, separately. In fact, the molecules of the two species can not be transformed into each another.

As discussed in the case of a single chiral gas (see Appendix A), the molecules of the species 1 and 2 will occupy the eigenstate having the lowest energy

$$\begin{aligned} \mathcal{E}(\psi_1, \psi_2) = & -\sum_{i=1}^2 \frac{\Delta E_i}{2} \langle \psi_i, \sigma_i^x \psi_i \rangle \\ & - \sum_{i=1}^2 \sum_{j=1}^2 \frac{G_{ij}}{2N_j} \langle \psi_i, \sigma_i^z \psi_i \rangle \langle \psi_j, \sigma_j^z \psi_j \rangle. \end{aligned} \quad (16)$$

In virtue of the symmetry property $G_{12}/N_2 = G_{21}/N_1$, the above energy is a constant of motion of the infinite-dimensional Hamiltonian system

$$i\hbar \frac{d}{dt} \psi_1 = h_1(\psi_1, \psi_2) \psi_1,$$

$$i\hbar \frac{d}{dt} \psi_2 = h_2(\psi_1, \psi_2) \psi_2.$$

Notice, in fact, that $\delta \mathcal{E}(\psi_1, \psi_2) / \delta \bar{\psi}_i = h_i(\psi_1, \psi_2) \psi_i$.

To solve the eigenvalue problem (15), we write

$$\psi_i = a_i \varphi_+^{(i)} + b_i \varphi_-^{(i)}, \quad i = 1, 2. \quad (18)$$

The coefficients a_i and b_i can be chosen real and are normalized to the number of molecules of each species, $a_i^2 + b_i^2 = N_i$. Up to an irrelevant global sign, we can also choose a_1 and a_2 non-negative. By inserting the expressions

(18) into Eq. (15), we find that a_1, b_1, a_2, b_2 are the solutions of the system of equations

$$\Delta E_i a_i b_i = \sum_{j=1}^2 2g_{ij} (a_i^2 - b_i^2) a_j b_j, \quad i = 1, 2 \quad (19)$$

where $g_{ij} = G_{ij}/N_j$. Once a solution of this system is found, the corresponding energy can be evaluated as

$$\mathcal{E} = -\sum_{i=1}^2 \frac{\Delta E_i}{2} (a_i^2 - b_i^2) - \sum_{i=1}^2 \sum_{j=1}^2 2g_{ij} a_i b_i a_j b_j.$$

It is convenient to discuss the solutions of Eq. (19) in function of the parameter $P \in [0, \infty)$. In fact, the matrix elements g_{ij} are proportional to the pressure. For any value of P , Eq. (19) admits solutions such that $a_1 b_1 = 0$ and $a_2 b_2 = 0$. There are four different solutions satisfying this condition and the normalization rule (see Table II). The solution

$$a_1 = \sqrt{N_1}, \quad b_1 = 0, \quad a_2 = \sqrt{N_2}, \quad b_2 = 0 \quad (20)$$

is that with the lowest energy $\mathcal{E} = -N(x_1 \Delta E_1/2 + x_2 \Delta E_2/2)$. We name this solution d_{++} because it corresponds to molecules of both species in a delocalized symmetric configuration.

If $a_1 b_1 = 0$ and $a_2 b_2 \neq 0$ or, vice versa, $a_1 b_1 \neq 0$ and $a_2 b_2 = 0$, Eq. (19) has no solutions. In fact, if $a_1 b_1 = 0$, then $a_1^2 - b_1^2 = \pm N_1$ and Eq. (19) for $i = 1$ gives $0 = \pm 2g_{12} N_1 a_2 b_2$ which can not be solved for $a_2 b_2 \neq 0$.

Equation (19) admits solutions with $a_1 b_1 \neq 0$ and $a_2 b_2 \neq 0$ if and only if

$$\begin{aligned} & [\Delta E_1 - 2g_{11}(a_1^2 - b_1^2)] [\Delta E_2 - 2g_{22}(a_2^2 - b_2^2)] \\ & - 4g_{12}g_{21}(a_1^2 - b_1^2)(a_2^2 - b_2^2) = 0. \end{aligned} \quad (21)$$

In fact, think of Eq. (19) as a linear homogeneous system of equations in the two unknowns $a_1 b_1$ and $a_2 b_2$. This system admits a nontrivial solution $(a_1 b_1, a_2 b_2) \neq (0, 0)$ if and only if its determinant is 0, namely, Eq. (21). Any nontrivial solution is necessarily of the form $a_1 b_1 \neq 0$ and $a_2 b_2 \neq 0$ because we have already established that Eq. (19) does not have solutions with just one term between $a_1 b_1$ and $a_2 b_2$ equal to 0.

If (a_1, b_1, a_2, b_2) is a solution of Eq. (19), that is true also for $(a_1, -b_1, a_2, -b_2)$ and these two solutions have the same energy. Therefore, each eigenstate obtained for $a_1 b_1 \neq 0$ and $a_2 b_2 \neq 0$ has a twofold degeneracy.

Observing that $g_{11}g_{22} - g_{12}g_{21} = 0$, Eq. (21) can be rewritten as

$$\begin{aligned} & 4g_{11}a_1^2 \Delta E_2 + 4g_{22}a_2^2 \Delta E_1 \\ & = 2g_{11}N_1 \Delta E_2 + 2g_{22}N_2 \Delta E_1 + \Delta E_1 \Delta E_2. \end{aligned} \quad (22)$$

The left-hand side of Eq. (22) is manifestly positive, therefore, we must conclude that also the right-hand side is so. In terms of P , remember that $g_{ij} \propto P$, this condition implies that the pressure has to be larger than the critical value

$$P_{\text{cr}} = \left(\sum_{i=1}^2 \frac{2x_i \gamma_{ii}}{\Delta E_i} \right)^{-1}, \quad (23)$$

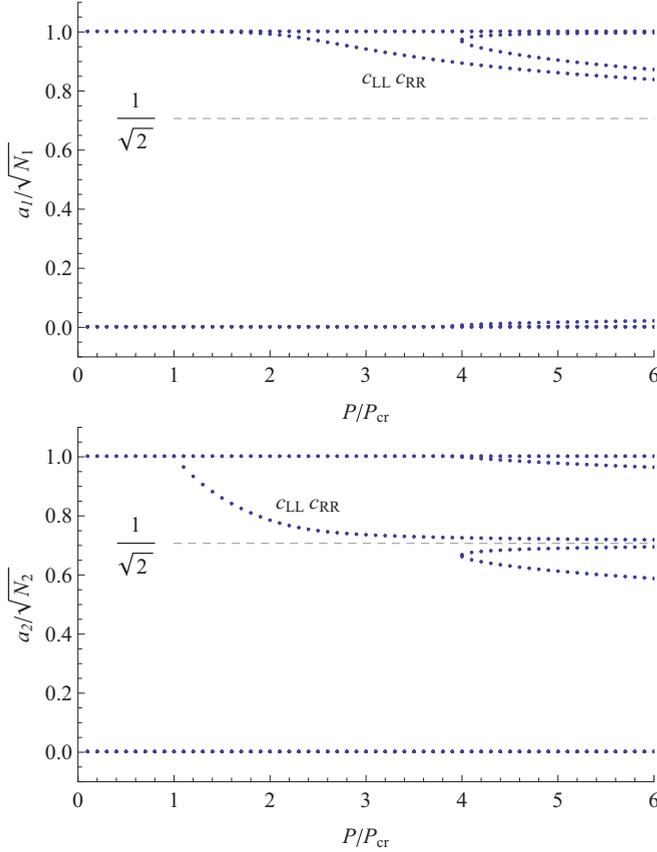


FIG. 3. (Color online) Coefficients $a_1/\sqrt{N_1}$ and $a_2/\sqrt{N_2}$ defining the molecular states ψ_1, ψ_2 of a two-species mixture as a function of P/P_{cr} . The coefficients have been obtained by solving numerically Eq. (19) in the case of a $\text{NH}_3\text{-ND}_3$ mixture (ND_3 is species $i = 2$) with $x_2 = 0.1$ at temperature $T = 300$ K. The coefficients bifurcating at $P = P_{\text{cr}}$ and tending for $P \gg P_{\text{cr}}$ to $1/\sqrt{2}$ (dashed line) describe two degenerate molecular states, named c_{LL} and c_{RR} , with molecules of both species in a chiral configuration of type L or R . Notice further bifurcations appearing at $P \simeq 4P_{\text{cr}}$, they correspond to stationary states of higher energy.

where we set

$$\gamma_{ij} = \frac{N}{P} g_{ij} = \frac{N}{N_j P} G_{ij} = \frac{4\pi}{9} \frac{\mu_i^2 \mu_j^2}{(4\pi \epsilon_0 k_B T)^2 d_{ii}^3}. \quad (24)$$

For $x_1 = 1$ or $x_2 = 1$, Eq. (23) reduces to the critical pressure (4) for the single species 1 or 2.

In conclusion, similarly to the case of a single chiral gas, it exists a critical pressure P_{cr} and a quantum phase transition taking place at $P = P_{\text{cr}}$. For $0 < P < P_{\text{cr}}$, the lowest-energy stationary state of the mixture is the delocalized d_{++} configuration given by Eq. (20). At $P = P_{\text{cr}}$ a bifurcation occurs and two new energy-degenerate stationary states appear (see Fig. 3 for an example). We call them c_{LL} and c_{RR} because they correspond to molecules of both species in a chiral configuration of type L or R (see Table II), achieving a complete localization for $P \gg P_{\text{cr}}$. The value of P_{cr} is given by Eq. (23). This formula says that the inverse critical pressure of the mixture is the fraction-weighted average of the inverse

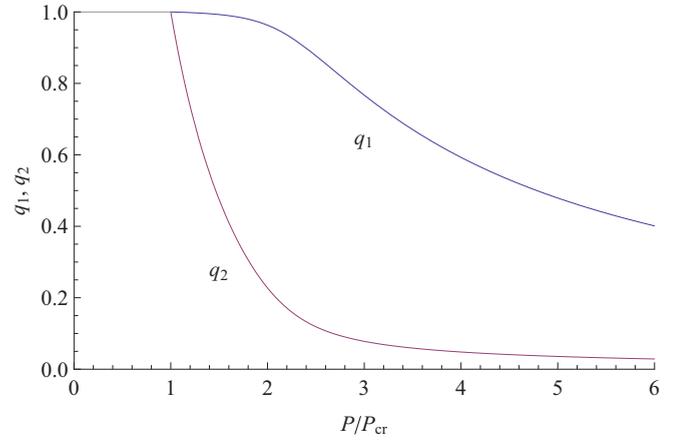


FIG. 4. (Color online) Parameters q_1, q_2 encoding the difference between the delocalized symmetric state d_{++} and the chiral states c_{LL} and c_{RR} of Table II evaluated numerically for the same mixture of Fig. 3.

critical pressures of its components

$$\frac{1}{P_{\text{cr}}} = \sum_{i=1}^2 x_i \frac{1}{P_{\text{cr}}^{(i)}}, \quad P_{\text{cr}}^{(i)} = \frac{\Delta E_i}{2\gamma_{ii}}. \quad (25)$$

The difference between the lowest-energy stationary solutions of the two phases, namely d_{++} and c_{LL}, c_{RR} , can be entirely encoded in the parameters

$$q_i = \begin{cases} 1, & P < P_{\text{cr}}, \\ 2a_i^2/N_i - 1, & P > P_{\text{cr}}, \end{cases} \quad i = 1, 2$$

(see Table II). An example of the behavior of q_1 and q_2 as a function of the pressure is shown in Fig. 4. Each parameter q_i vanishes for $P \rightarrow \infty$. More precisely, by using Eq. (19) it is simple to show that at the leading order for P large one has

$$q_i = \frac{\gamma_{ii}}{\sum_{j=1}^2 \gamma_{ij} x_j} \frac{P_{\text{cr}}^{(i)}}{P}, \quad (26)$$

where $P_{\text{cr}}^{(i)}$ is the critical pressure of the i th species as given by Eq. (25).

B. Excitation energies: Normal modes, inversion frequencies

As in the case of a single chiral species, we can determine the excitation energies from the ground state of a binary mixture by evaluating the linear response to an external time-dependent perturbation representing an electromagnetic radiation. In detail, we modify the Hamiltonians (14) by adding for each species $i = 1, 2$ a perturbation of the form $\mu_i F(t) \sigma_i^z$ with the field $F(t) = F \cos(\omega t)$ sufficiently small so that effects of order $O(F^2)$ are negligible. The perturbation induces a modified time evolution of the unperturbed ground state of the system which we evaluate as follows.

For $P < P_{\text{cr}}$, the ground state of the mixture at zero external field is the symmetric delocalized state d_{++} defined by the coefficients (a_1, b_1, a_2, b_2) given by Eq. (20). For $P > P_{\text{cr}}$, the unperturbed mixture has two lowest-energy degenerate stationary states, namely the states c_{LL} and c_{RR} , defined by the two sets of coefficients (a_1, b_1, a_2, b_2) and $(a_1, -b_1, a_2, -b_2)$

given in Table II in terms of the parameters q_1, q_2 . For a racemic mixture, which is usually the case of concern, we may assume that the unperturbed ground state of species $i = 1, 2$ in the localized phase is represented by the *stationary* density matrix obtained by summing with equal weights the pure chiral states of types L and R :

$$\begin{aligned} \varrho_i^{(0)} &= \frac{1}{2} \begin{pmatrix} a_i \\ b_i \end{pmatrix} (a_i \quad b_i) + \frac{1}{2} \begin{pmatrix} a_i \\ -b_i \end{pmatrix} (a_i \quad -b_i) \\ &= \frac{N_i}{2} (\mathbb{1}_i + q_i \sigma_i^x). \end{aligned} \quad (27)$$

Since for $P < P_{\text{cr}}$ we have $q_1 = q_2 = 1$, Eq. (27) represents the ground-state density matrix of the species $i = 1, 2$ also in the delocalized phase. In conclusion, we can analyze simultaneously both phases $P \gtrless P_{\text{cr}}$ assuming that the unperturbed lowest-energy stationary state is given by the density matrices $\varrho_1^{(0)}, \varrho_2^{(0)}$ of Eq. (27).

Under the effect of the perturbation, the time evolution of the density matrices of the two species is governed by the equations

$$i\hbar \frac{d}{dt} \varrho_1(t) = [h_1(\varrho_1(t), \varrho_2(t)) + \mu_1 F(t) \sigma_1^z, \varrho_1(t)], \quad (28a)$$

$$i\hbar \frac{d}{dt} \varrho_2(t) = [h_2(\varrho_1(t), \varrho_2(t)) + \mu_2 F(t) \sigma_2^z, \varrho_2(t)], \quad (28b)$$

where the mean-field Hamiltonians $h_i(\varrho_1, \varrho_2)$, $i = 1, 2$, are the same as Eq. (14) only rewritten in terms of the density matrices ϱ_1, ϱ_2 :

$$h_i(\varrho_1, \varrho_2) = -\frac{\Delta E_i}{2} \sigma_i^x - \sum_{j=1}^2 g_{ij} \text{tr}(\sigma_j^z \varrho_j) \sigma_i^z. \quad (29)$$

The density matrix of the i th species at time t is written as

$$\varrho_i(t) = \varrho_i^{(0)} + x_i(t) \sigma_i^x + y_i(t) \sigma_i^y + z_i(t) \sigma_i^z. \quad (30)$$

Neglecting second-order terms in the perturbation, the Bloch vector $(x_i(t), y_i(t), z_i(t))$ is determined by the system of differential equations

$$\hbar \dot{x}_i'(t) = 0,$$

$$\hbar \dot{y}_i'(t) = \Delta E_i z_i(t) - \sum_{j=1}^2 2N_i q_i g_{ij} z_j(t) + N_i q_i \mu_i F(t),$$

$$\hbar \dot{z}_i'(t) = -\Delta E_i y_i(t)$$

obtained by plugging the definition (30) into Eq. (28).

We are interested in evaluating the electric dipole moments of each species $i = 1, 2$, namely,

$$p_i(t) = \mu_i \text{tr}(\sigma_i^z \varrho_i(t)) = 2\mu_i z_i(t).$$

From the differential equations for the Bloch vector, we find that the Fourier transforms $\tilde{p}_1(\omega), \tilde{p}_2(\omega)$ are given by the system of algebraic equations

$$\begin{aligned} (\hbar^2 \omega^2 - \Delta E_i^2) \tilde{p}_i(\omega) + \sum_{j=1}^2 2N_i q_i \Delta E_i g_{ij} \tilde{p}_j(\omega) \\ = 2\mu_i^2 N_i q_i \Delta E_i \tilde{F}(\omega), \quad i = 1, 2 \end{aligned} \quad (31)$$

where $\tilde{F}(\omega)$ is the Fourier transform of the applied field. The frequency-dependent electric susceptibility of the i th species is finally evaluated as the ratio between the Fourier transform of the polarization density of that species and the Fourier transform of the applied field,

$$\chi_i(\omega) = \frac{\tilde{p}_i(\omega)/(N/\rho)}{\varepsilon_0 \tilde{F}(\omega)},$$

where N/ρ is the volume occupied by the mixture and ε_0 the vacuum dielectric constant [20]. As usual, the density of the mixture at pressure P and temperature T is assumed to be $\rho = P/k_B T$. By determining $\tilde{p}_1(\omega)$ and $\tilde{p}_2(\omega)$ from Eq. (31), we find that the susceptibility of the mixture $\chi = \chi_1 + \chi_2$ is given by

$$\chi(\omega) = \frac{\rho}{\varepsilon_0} \frac{C(\omega)}{D(\omega)}, \quad (32)$$

where

$$\begin{aligned} C(\omega) &= \xi_1 \mu_1^2 [\hbar^2 \omega^2 - \Delta E_2^2 + \xi_2 (\gamma_{22} - \gamma_{12}) P] \\ &\quad + \xi_2 \mu_2^2 [\hbar^2 \omega^2 - \Delta E_1^2 + \xi_1 (\gamma_{11} - \gamma_{21}) P], \end{aligned} \quad (33)$$

$$\begin{aligned} D(\omega) &= (\hbar^2 \omega^2 - \Delta E_1^2 + \xi_1 \gamma_{11} P) \\ &\quad \times (\hbar^2 \omega^2 - \Delta E_2^2 + \xi_2 \gamma_{22} P) - \xi_1 \xi_2 \gamma_{12} \gamma_{21} P^2, \end{aligned} \quad (34)$$

$$\xi_i = 2x_i q_i \Delta E_i, \quad i = 1, 2. \quad (35)$$

The poles of the linear-response function (32) provide the excitation energies from the ground state predicted by our mean-field model [21]. It is worth to explore first two limit cases.

For noninteracting molecules, namely $\gamma_{ij} = 0$, $i, j = 1, 2$, we have

$$\chi(\omega) = \frac{\rho}{\varepsilon_0} \left(\frac{\xi_1 \mu_1^2}{\hbar^2 \omega^2 - \Delta E_1^2} + \frac{\xi_2 \mu_2^2}{\hbar^2 \omega^2 - \Delta E_2^2} \right).$$

As expected, the response to an electromagnetic radiation incident on the mixture would, in this case, provide excitation energies ΔE_1 and ΔE_2 corresponding to the inversion of isolated molecules of species 1 and 2.

For a gas with just one chiral species, let us say $x_2 = 0$, Eq. (32) reduces to

$$\chi(\omega) = \frac{\rho \mu_1^2}{\varepsilon_0} \frac{2q_1 \Delta E_1}{\hbar^2 \omega^2 - (\Delta E_1^2 - 2q_1 \Delta E_1 \gamma_{11} P)}.$$

In this case, we also have [22] $q_1 = 1$ for $P < P_{\text{cr}}$ and $q_1 = \Delta E_1 / (2G_{11})$ for $P > P_{\text{cr}}$, where $G_{11} = \gamma_{11} P$, so that we recover the result of Eq. (B1). The same conclusion is obtained if we consider a single chiral gas as the mixture of two identical species with arbitrary fractions x_1 and x_2 such that $x_1 + x_2 = 1$.

For a general mixture, no partial cancellation of zeros between numerator and denominator of $\chi(\omega)$ takes place as in the above two limit cases. The poles of the electric susceptibility coincide with the zeros of $D(\omega)$. By using the property $\gamma_{11} \gamma_{22} - \gamma_{12} \gamma_{21} = 0$, we find that the biquadratic

equation $D(\omega) = 0$ has solutions with modulus $\bar{\omega}_{\pm}$ given by

$$2\hbar^2\bar{\omega}_{\pm}^2 = A_{12} \pm \sqrt{A_{12}^2 - 4B_{12}}, \quad (36)$$

where

$$A_{12} = \Delta E_1^2 + \Delta E_2^2 - (\xi_1\gamma_{11} + \xi_2\gamma_{22})P,$$

$$B_{12} = \Delta E_1^2\Delta E_2^2 - (\xi_1\gamma_{11}\Delta E_2^2 + \xi_2\gamma_{22}\Delta E_1^2)P.$$

Clearly, the excitation energies of the mixture $\hbar\bar{\omega}_{\pm}$ are functions of the pressure.

At $P = 0$, the normal modes represent the inversion of isolated molecules of species 1 or 2, namely,

$$\hbar\bar{\omega}_{\pm}(0) = \Delta E_{i_{\pm}},$$

where $i_+ = 1$ and $i_- = 2$ if $\Delta E_1 > \Delta E_2$ and $i_+ = 2$ and $i_- = 1$ if $\Delta E_2 > \Delta E_1$.

In the delocalized phase $0 < P < P_{\text{cr}}$, we have

$$B_{12}(P) = \Delta E_1^2\Delta E_2^2(1 - P/P_{\text{cr}}),$$

in virtue of the fact that $q_1 = q_2 = 1$. For the same reason, we also have that ξ_1 and ξ_2 are constant in this phase so that $A_{12}(P)$ decreases linearly with P . As a result, we find that $\hbar\bar{\omega}_{\pm}(P)$ decrease from their $P = 0$ value according to

$$\hbar\bar{\omega}_{\pm}(P) \simeq \Delta E_{i_{\pm}} \sqrt{1 - \frac{P}{P_{\text{cr}}^{(i_{\pm})}}}.$$

These approximated relations, which are merely the inversion frequency laws for the pure species [see Eq. (C1)], are valid for P small. The larger is the fraction of the species i_{\pm} , the wider is the range of P where the approximation is adequate.

At $P = P_{\text{cr}}$, we have $B_{12}(P_{\text{cr}}) = 0$ and, according to Eq. (36), the energy $\hbar\bar{\omega}_-$ vanishes with an infinite slope. The energy of the other mode attains the finite value $\hbar\bar{\omega}_+ = \sqrt{A_{12}(P_{\text{cr}})}$.

In the localized phase $P > P_{\text{cr}}$, where $q_i = 2a_i^2/N_i - 1$, $i = 1, 2$, with a_1^2 and a_2^2 satisfying Eq. (22), we have $B_{12}(P) = 0$ for any value of P . It follows that $\hbar\bar{\omega}_- = 0$ throughout this phase. The energy of the other mode persists in decreasing and for $P \gg P_{\text{cr}}$ approaches the asymptotic value

$$\hbar\bar{\omega}_+^{\text{as}} = \sqrt{\frac{\Delta E_1^2\gamma_{12}x_2}{\gamma_{11}x_1 + \gamma_{12}x_2} + \frac{\Delta E_2^2\gamma_{21}x_1}{\gamma_{22}x_2 + \gamma_{21}x_1}}. \quad (37)$$

This value corresponds to $\sqrt{A_{12}}$ evaluated with the leading-order expressions of q_1, q_2 as in Eq. (26).

In Figs. 5 and 6, we show the excitation energies $\hbar\bar{\omega}_{\pm}$ calculated for a NH_3 - ND_3 mixture with 10% and 0.01% deuterated ammonia fraction, respectively.

C. Consistency of the model: Absorption coefficient

We have already discussed the consistency of our model by considering two limiting cases in which it must recover the single gas case. In fact, we have observed that the susceptibility of a binary mixture reduces to that of a single chiral gas in the limit of fraction of one species tending to zero or in the limit in which the parameters defining the two species become equal. Here, we study in deeper details this limiting behavior by taking into account the absorption coefficient associated with the evaluated susceptibility.

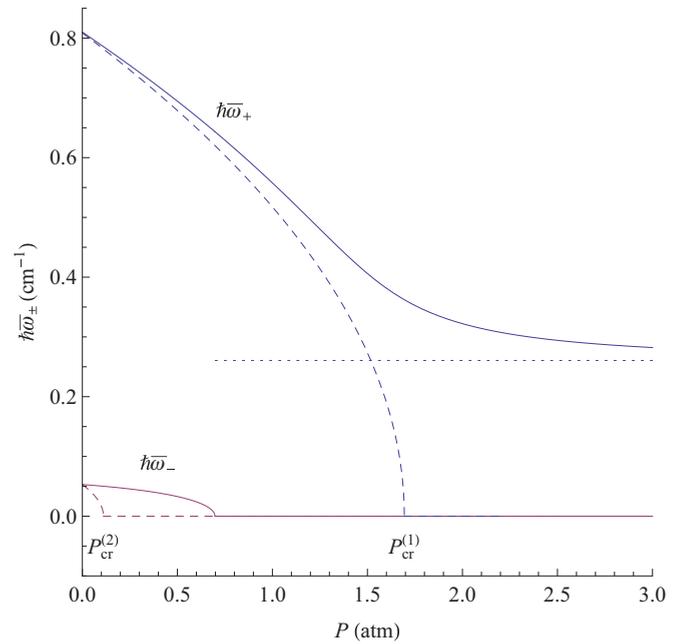


FIG. 5. (Color online) Energies $\hbar\bar{\omega}_{\pm}$ of the excitation normal modes as a function of pressure P in the case of a NH_3 - ND_3 mixture (ND_3 is species $i = 2$) with $x_2 = 0.1$ at $T = 300$ K. The horizontal dotted line is the asymptotic value $\hbar\bar{\omega}_+^{\text{as}}$. The dashed lines which vanish at $P_{\text{cr}}^{(1)} = 1.69$ atm and $P_{\text{cr}}^{(2)} = 0.11$ atm correspond to the inversion frequencies of pure species. The critical pressure of the mixture, the point where $\hbar\bar{\omega}_-$ vanishes, is $P_{\text{cr}} = 0.70$ atm. Energy is measured in cm^{-1} .

According to the Beer-Lambert law, the intensity of a monochromatic radiation of angular frequency ω propagating

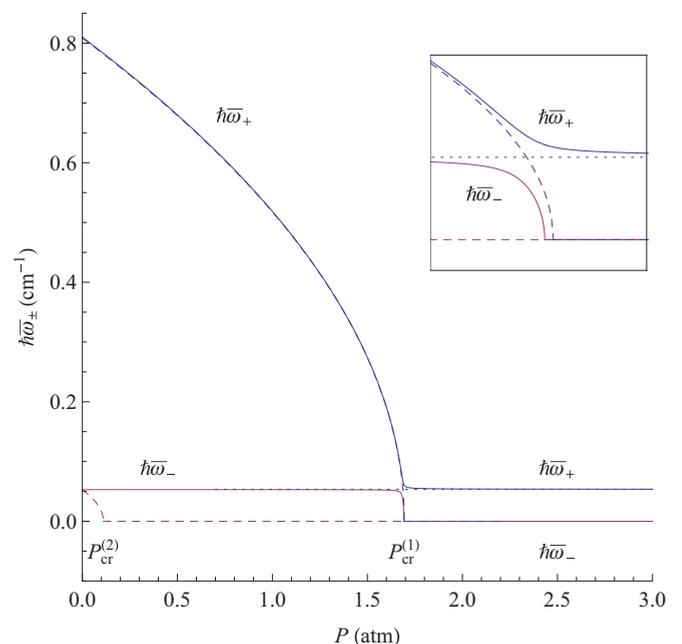


FIG. 6. (Color online) As in Fig. 5 for $x_2 = 0.0001$. For such small value of x_2 the critical pressure of the mixture is $P_{\text{cr}} \simeq P_{\text{cr}}^{(1)}$ and we have $\hbar\bar{\omega}_+^{\text{as}} \simeq \Delta E_{i_-}$. Inset is a zoomed-in view of the region $P \simeq P_{\text{cr}}$.

for a length ℓ into the mixture is decreased by a factor $e^{-\kappa(\omega)\ell}$ due to the excitation of the normal modes. Neglecting deexcitation from these modes, i.e., spontaneous and stimulated reemission of radiation, the absorption coefficient is

$$\kappa(\omega) = \frac{\omega}{c} \text{Im} \chi(\omega), \quad (38)$$

with c speed of light and $\chi(\omega)$ as in Eq. (32). The imaginary part of susceptibility is evaluated with the prescription $\omega \rightarrow \omega - i\eta$ where $\eta \rightarrow 0^+$. The result is

$$\begin{aligned} \kappa(\omega) = & I_+ [\delta(\hbar\omega - \hbar\bar{\omega}_+) + \delta(\hbar\omega + \hbar\bar{\omega}_+)] \\ & + I_- [\delta(\hbar\omega - \hbar\bar{\omega}_-) + \delta(\hbar\omega + \hbar\bar{\omega}_-)], \end{aligned} \quad (39)$$

where the intensities I_{\pm} are

$$I_{\pm} = \frac{\pi\rho}{2\varepsilon_0 c \hbar} \frac{C(\bar{\omega}_{\pm})}{\hbar^2 \bar{\omega}_{\pm}^2 - \hbar^2 \bar{\omega}_{\mp}^2}, \quad (40)$$

with $C(\omega)$ given by Eq. (33). These intensities depend on the pressure and for $P \rightarrow 0$ at the leading order they are

$$I_{\pm}(P) = x_{i_{\pm}} \frac{\pi \Delta E_{i_{\pm}} \mu_{i_{\pm}}^2}{\varepsilon_0 c \hbar k_B T} P. \quad (41)$$

We have assumed, as usual, $\rho = P/(k_B T)$ and used the property $\hbar\bar{\omega}_{\pm} \rightarrow \Delta E_{i_{\pm}}$ for $P \rightarrow 0$. Thus, when the density vanishes and the intermolecular interactions can be neglected, the absorption coefficient of the mixture is the sum of the absorption coefficients of the two isolated species weighted by the corresponding fractions.

Note that for noninteracting molecules, i.e., $\gamma_{ij} = 0$, $i, j = 1, 2$, the intensities I_{\pm} are as in Eq. (41), i.e., the absorption coefficient grows indefinitely with the pressure. On the other hand, for interacting molecules we obtain that for $P \rightarrow \infty$ the absorption coefficient approaches a constant value with asymptotic intensities

$$\begin{aligned} I_+^{\text{as}} = & x_1 \frac{\pi \Delta E_1 \mu_1^2}{\varepsilon_0 c \hbar k_B T} P_{\text{cr}}^{(1)} \frac{\gamma_{11}}{\gamma_{11} x_1 + \gamma_{12} x_2} \left[1 - \left(\frac{\Delta E_2}{\hbar\bar{\omega}_+^{\text{as}}} \right)^2 \right] \\ & + x_2 \frac{\pi \Delta E_2 \mu_2^2}{\varepsilon_0 c \hbar k_B T} P_{\text{cr}}^{(2)} \frac{\gamma_{22}}{\gamma_{22} x_2 + \gamma_{21} x_1} \left[1 - \left(\frac{\Delta E_1}{\hbar\bar{\omega}_+^{\text{as}}} \right)^2 \right], \\ I_-^{\text{as}} = & x_1 \frac{\pi \Delta E_1 \mu_1^2}{\varepsilon_0 c \hbar k_B T} P_{\text{cr}}^{(1)} \frac{\gamma_{11}}{\gamma_{11} x_1 + \gamma_{12} x_2} \left(\frac{\Delta E_2}{\hbar\bar{\omega}_+^{\text{as}}} \right)^2 \\ & + x_2 \frac{\pi \Delta E_2 \mu_2^2}{\varepsilon_0 c \hbar k_B T} P_{\text{cr}}^{(2)} \frac{\gamma_{22}}{\gamma_{22} x_2 + \gamma_{21} x_1} \left(\frac{\Delta E_1}{\hbar\bar{\omega}_+^{\text{as}}} \right)^2. \end{aligned}$$

To understand the limit of the absorption coefficient for, e.g., $x_2 \rightarrow 0$, observe that when the fraction of species 2 vanishes we have $P_{\text{cr}} \rightarrow P_{\text{cr}}^{(1)}$ and the limit frequencies are

$$\begin{aligned} \hbar\bar{\omega}_+ & \rightarrow \begin{cases} \Delta E_1 \sqrt{1 - P/P_{\text{cr}}^{(1)}}, & P < P_{\text{cr}}^{(1)} \\ \Delta E_2, & P > P_{\text{cr}}^{(1)} \end{cases} \\ \hbar\bar{\omega}_- & \rightarrow \begin{cases} \Delta E_2, & P < P_{\text{cr}}^{(1)} \\ 0, & P > P_{\text{cr}}^{(1)} \end{cases} \end{aligned}$$

if $\Delta E_1 > \Delta E_2$, whereas for $\Delta E_2 > \Delta E_1$ we have

$$\begin{aligned} \hbar\bar{\omega}_+ & \rightarrow \Delta E_2, \\ \hbar\bar{\omega}_- & \rightarrow \begin{cases} \Delta E_1 \sqrt{1 - P/P_{\text{cr}}^{(1)}}, & P < P_{\text{cr}}^{(1)} \\ 0, & P > P_{\text{cr}}^{(1)}. \end{cases} \end{aligned}$$

From Eq. (40) it follows that

$$\begin{aligned} I_+ & \rightarrow \frac{\pi \Delta E_1 \mu_1^2}{\varepsilon_0 c \hbar k_B T} \begin{cases} P, & P < P_{\text{cr}}^{(1)} \\ 0, & P > P_{\text{cr}}^{(1)} \end{cases} \\ I_- & \rightarrow \frac{\pi \Delta E_1 \mu_1^2}{\varepsilon_0 c \hbar k_B T} \begin{cases} 0, & P < P_{\text{cr}}^{(1)} \\ P_{\text{cr}}^{(1)}, & P > P_{\text{cr}}^{(1)} \end{cases} \end{aligned}$$

if $\Delta E_1 > \Delta E_2$, whereas for $\Delta E_2 > \Delta E_1$ we have

$$\begin{aligned} I_+ & \rightarrow 0, \\ I_- & \rightarrow \frac{\pi \Delta E_1 \mu_1^2}{\varepsilon_0 c \hbar k_B T} \begin{cases} P, & P < P_{\text{cr}}^{(1)} \\ P_{\text{cr}}^{(1)}, & P > P_{\text{cr}}^{(1)}. \end{cases} \end{aligned}$$

In both cases, we recover the intensity of the pure chiral gas 1, increasing linearly with P in the delocalized phase and locked at a constant value in the localized one.

In the limit $x_1 \rightarrow 0$, one has similar formulas which can be obtained from the above ones by exchanging the indices $1 \leftrightarrow 2$.

An example of the behavior of the intensities I_{\pm} as a function of pressure P is illustrated in Figs. 7 and 8 for the same $\text{NH}_3\text{-ND}_3$ mixtures considered in Figs. 5 and 6, respectively. In this case, we have $\Delta E_1 > \Delta E_2$ and the fraction x_2 decreases from 0.1, Figs. 5 and 7, to 0.0001, Figs. 6 and 8. The dominant intensity I_+ or I_- is mainly due to the more abundant species $i = 1$.

We now discuss the limit in which $\Delta E_1, \Delta E_2 \rightarrow \Delta E$, $\mu_1, \mu_2 \rightarrow \mu$, and $\gamma_{i,j} \rightarrow \gamma$, $i, j = 1, 2$, whereas x_1 and x_2 are arbitrary with $x_1 + x_2 = 1$. In this case, we have

$$\begin{aligned} \hbar\bar{\omega}_+ & \rightarrow \Delta E, \\ \hbar\bar{\omega}_- & \rightarrow \begin{cases} \Delta E \sqrt{1 - P/P_{\text{cr}}}, & P < P_{\text{cr}} \\ 0, & P > P_{\text{cr}} \end{cases} \end{aligned}$$

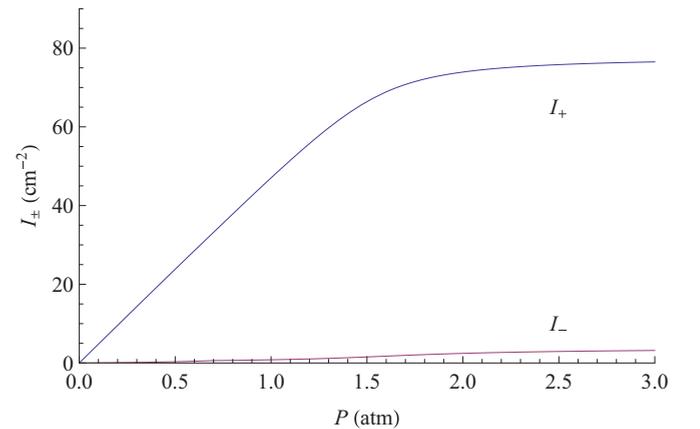


FIG. 7. (Color online) Intensities I_{\pm} of the absorption coefficient as a function of pressure P for the mixture of Fig. 5. Energy is measured in cm^{-1} and intensities, which have dimensions energy divided by length, are given in cm^{-2} .

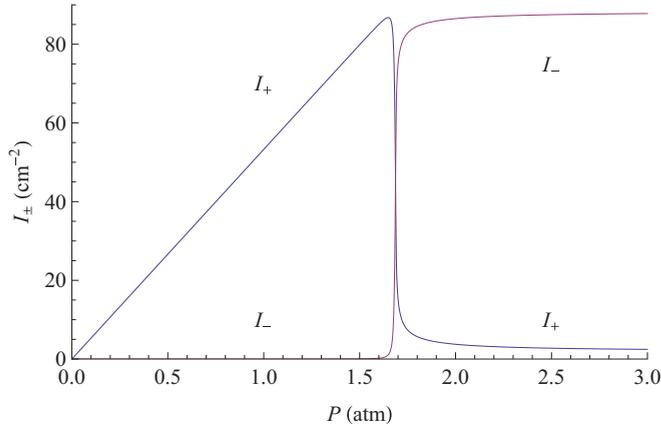


FIG. 8. (Color online) As in Fig. 7 for the mixture of Fig. 6.

where $P_{\text{cr}} = \Delta E / (2\gamma)$. It is simple to verify that

$$I_{+} \rightarrow 0,$$

$$I_{-} \rightarrow \frac{\pi \Delta E \mu^2}{\varepsilon_0 c \hbar k_B T} \begin{cases} P, & P < P_{\text{cr}} \\ P_{\text{cr}}, & P > P_{\text{cr}} \end{cases}$$

which is again the result for a single species characterized by the parameters ΔE , μ , and γ .

Due to line broadening, which in the microwave region of interest for a NH_3 - ND_3 mixture is mostly due to molecular scattering, the absorption coefficient discussed above can not be directly compared with that measured in an experiment. However, a test of the excitation energies (36) could be done in an indirect way as in [9–11]. In these experiments the spectrum of the absorption coefficient measured for NH_3 or ND_3 at different pressures was fitted by a Van Vleck–Weisskopf formula [23] in which the center line frequency is considered a fitting parameter. The results of the fit are in excellent agreement with the predictions of our model for a single chiral gas (see [7] or Appendix C). In the case of a NH_3 - ND_3 mixture, the situation is not different. If our model is correct, with a 10% ND_3 fraction one should measure an absorption spectrum, mainly due to the $\hbar\bar{\omega}_+$ excitation mode (see Fig. 7), centered at a frequency which at high pressures approaches the value of 0.26 cm^{-1} (see Fig. 5). This is a striking difference with respect to the case of a pure NH_3 gas in which the center line frequency of the absorption spectrum vanishes for $P > 1.69 \text{ atm}$. Also, the behavior of $\hbar\bar{\omega}_-(P)$ is rather different from the inversion frequency of pure ND_3 . In fact, the two frequencies vanish at 0.70 and 0.11 atm , respectively. However, this effect should be more difficult to measure as the intensity I_- is much lower than I_+ (see Fig. 7).

VI. FINAL REMARKS

Our approach to the existence of chiral molecules is based on ideas of equilibrium statistical mechanics. One may be surprised by the presence of a quantum phase transition at room temperatures. We emphasize that the transition takes place only in the inversion degrees of freedom. The dynamics of these degrees of freedom is affected by temperature only through the values of the coupling constants. A derivation of our approach from first principles is an open question. As

we have discussed, in the case of a pure gas of ammonia or deuterated ammonia, our model compares very well with experimental results.

The problem of existence of chiral molecules has been approached also from a dynamical point of view [24–26] in terms of the quantum linear evolution with a Lindblad term. The question asked by these authors is how long a molecule in a chiral localized state remains in this state considering the interaction with the environment. This question had already been posed by Hund [1] without, however, any quantitative estimate. In Refs. [24,25], a calculation *ab initio* is discussed exploiting a mechanism whose basic idea goes back to [27,28]: through repeated scatterings in a host gas, a molecule is blocked in a localized state. A detailed analysis of the decoherence of a two-state tunneling molecule due to collisions with a host gas is given in [26] in terms of a succession of quantum states of the molecule satisfying the conditions for a consistent family of histories.

Effective nonlinearities, closer to our interpretation, were considered in a dynamical context by [29] and qualitatively connected to the disappearance of the inversion line. However, no quantitative estimate was attempted. In [30], dissipative effects are included in a nonlinear time-dependent model obtaining qualitative conclusions similar to [7]. What is missing is a theory of the parameters of the model.

An important test of the present theory is to verify the shift of the critical pressure depending on the percentage of the two species in a binary mixture, e.g., NH_3 - ND_3 . As we have shown, an addition of 10% of ND_3 is sufficient to halve the critical pressure of pure NH_3 and to appreciably change the dependence on pressure of the inversion frequencies of both species.

The interpretation of the experimental data [9–11] is based on the Van Vleck–Weisskopf formula. The inversion line measured at sufficiently high pressures consists actually of a band of lines close to each other arising from different angular momentum states. At low pressures, these lines can be resolved [31]. We may ask the question whether this case can be discussed in terms of a mixture of different prechiral gases corresponding to ammonia molecules in different angular momentum states and study the crossover to higher pressures.

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APPENDIX A: STATIONARY STATES OF A CHIRAL GAS

The nonlinear eigenvalue problem associated with Eq. (2) and the normalization condition, namely,

$$h(\psi_\lambda)\psi_\lambda = \lambda\psi_\lambda, \quad \langle \psi_\lambda, \psi_\lambda \rangle = N, \quad (\text{A1})$$

where

$$h(\psi) = -\frac{\Delta E}{2}\sigma^x - \frac{G}{N}\langle \psi, \sigma^z \psi \rangle \sigma^z,$$

has different solutions depending on the value of the ratio $G/\Delta E$. To see it, let us write

$$\psi_\lambda = a_\lambda \varphi_+ + b_\lambda \varphi_-.$$

The coefficients a_λ and b_λ can be chosen real and are normalized to the number of molecules in the gas $a_\lambda^2 + b_\lambda^2 = N$. By inserting this expression into Eq. (A1), we find that a_λ, b_λ are the solutions of the equation

$$\Delta E a_\lambda b_\lambda = \frac{G}{N} (a_\lambda^2 - b_\lambda^2) 2a_\lambda b_\lambda. \quad (\text{A2})$$

Once a solution of this system is found, the corresponding eigenvalue is given by

$$\lambda N = -\frac{\Delta E}{2} (a_\lambda^2 - b_\lambda^2) - \frac{4G}{N} a_\lambda^2 b_\lambda^2.$$

For any value of G , Eq. (A2) always admits solutions such that $a_\lambda b_\lambda = 0$. Up to an irrelevant sign, there are two different solutions which satisfy this condition and the normalization rule, namely, the delocalized eigenstates

$$\psi_{\lambda_1} = \sqrt{N} \varphi_+, \quad \lambda_1 = -\Delta E/2, \quad (\text{A3})$$

$$\psi_{\lambda_2} = \sqrt{N} \varphi_-, \quad \lambda_2 = +\Delta E/2. \quad (\text{A4})$$

If $G > \Delta E/2$, there appear two further solutions such that $a_\lambda b_\lambda \neq 0$, namely, the roots of

$$2a_\lambda^2/N - 1 = \Delta E/(2G). \quad (\text{A5})$$

The corresponding eigenstates are

$$\psi_{\lambda_3} = \sqrt{N} \left(\sqrt{\frac{1}{2} + \frac{\Delta E}{4G}} \varphi_+ + \sqrt{\frac{1}{2} - \frac{\Delta E}{4G}} \varphi_- \right), \quad (\text{A6})$$

$$\lambda_3 = -G$$

$$\psi_{\lambda_4} = \sqrt{N} \left(\sqrt{\frac{1}{2} + \frac{\Delta E}{4G}} \varphi_+ - \sqrt{\frac{1}{2} - \frac{\Delta E}{4G}} \varphi_- \right) \quad (\text{A7})$$

$$\lambda_4 = -G.$$

We call these states chiral in the sense that $\psi_{\lambda_3} = \sigma^x \psi_{\lambda_4}$ and $\psi_{\lambda_4} = \sigma^x \psi_{\lambda_3}$. In the limit $G \gg \Delta E$, the eigenstates ψ_{λ_3} and ψ_{λ_4} approach the localized states $\sqrt{N} \varphi_L$ and $\sqrt{N} \varphi_R$, respectively.

The states ψ_λ determined above are the stationary solutions $\psi(t) = \exp(-i\lambda t/\hbar) \psi_\lambda$ of the time-dependent nonlinear Schrödinger equation

$$i\hbar \frac{d}{dt} \psi(t) = h(\psi) \psi(t)$$

and the eigenvalue λ is the Lagrange multiplier fixing the conservation of the number of molecules. Associated with any solution $\psi(t)$ of this equation there is a conserved energy given by

$$\mathcal{E}(\psi) = -\frac{\Delta E}{2} \langle \psi, \sigma^x \psi \rangle - \frac{G}{2N} \langle \psi, \sigma^z \psi \rangle^2.$$

The value of this functional calculated at the stationary solutions (A3)–(A7), i.e.,

$$\mathcal{E}(\psi_\lambda) = -\frac{\Delta E}{2} (a_\lambda^2 - b_\lambda^2) - \frac{2G}{N} a_\lambda^2 b_\lambda^2,$$

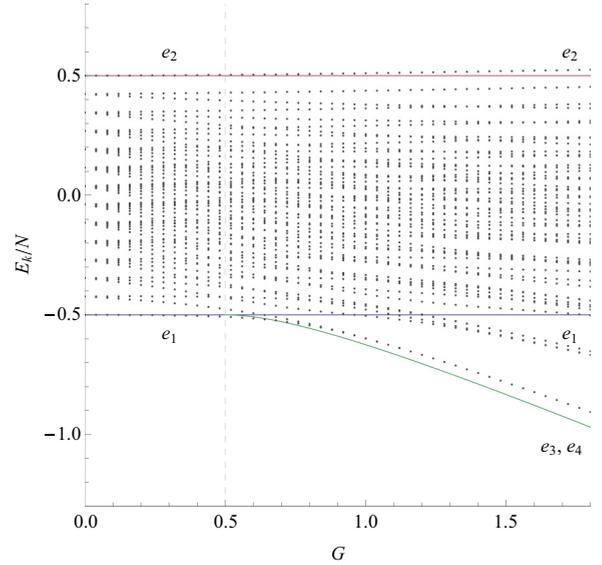


FIG. 9. (Color online) Eigenvalues E_k , $k = 1, \dots, 2^N$, divided by N , of the N -body Hamiltonian of Eq. (1) with $g_{ij} = G/N$ and $N = 13$ calculated numerically for different values of G (dots). The solid lines are the single-molecule energies $e_i = \mathcal{E}(\psi_{\lambda_i})/N$ associated with the mean-field stationary states ψ_{λ_i} , $i = 1, \dots, 4$.

provides the corresponding single-molecule energies $e_i = \mathcal{E}(\psi_{\lambda_i})/N$, $i = 1, \dots, 4$,

$$e_1 = -\frac{\Delta E}{2},$$

$$e_2 = +\frac{\Delta E}{2},$$

$$e_3 = e_4 = -\frac{\Delta E}{2} - \frac{1}{2G} \left(\frac{\Delta E}{2} - G \right)^2.$$

These energies are plotted in Fig. 9 as a function of G . The molecular state effectively assumed by the gas is that with the minimal energy, namely, the symmetric delocalized state ψ_{λ_1} for $G < \Delta E/2$, or one of the two degenerate chiral states ψ_{λ_3} , ψ_{λ_4} for $G > \Delta E/2$.

The above results imply a bifurcation of the mean-field ground state at a critical interaction strength $G_{\text{cr}} = \Delta E/2$. According to Eq. (3), this transition can be obtained for a given molecular species by increasing the gas pressure above the critical value P_{cr} given by Eq. (4).

APPENDIX B: EXCITATIONS FROM THE GROUND STATE

It is interesting to compare the mean-field molecular states described in the previous section with the eigenstates of the N -body model (1). In the latter case, the Hamiltonian is represented by a $2^N \times 2^N$ matrix which, if N is not too large, can be diagonalized numerically. For a meaningful comparison with the mean field we set $g_{ij} = G/N$. The eigenvalues obtained for $N = 13$ are shown in Fig. 9 as a function of G . We see that there is a strict correspondence between the smallest and largest eigenvalues of (1) and the smallest and largest conserved energies associated with the mean-field eigenstates of (2). Assuming that the eigenstates of (1) are

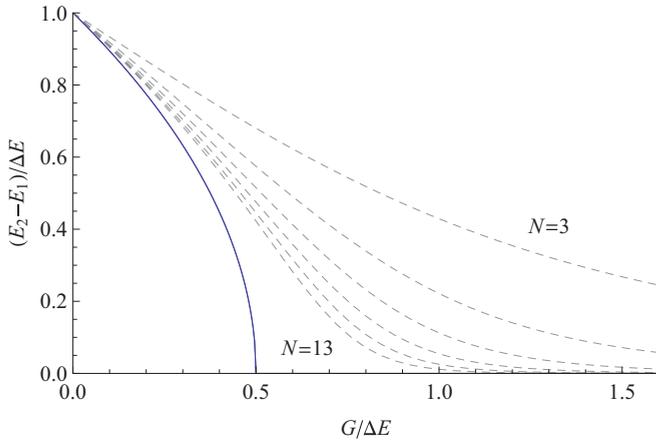


FIG. 10. (Color online) Energy gap $E_2 - E_1$ of the N -body Hamiltonian (1) with $g_{ij} = G/N$ and $N = 3, 5, 7, 9, 11, 13$ (dashed lines from top to bottom) as a function of the ratio $G/\Delta E$. The solid line represents $h\bar{\nu}/\Delta E$, where $\bar{\nu}$ is the inversion doubling frequency predicted by Eq. (B2).

ordered according to their magnitude $E_1 < E_2 < \dots, E_{2^N}$, we have

$$E_1 \simeq \begin{cases} \mathcal{E}(\psi_{\lambda_1}), & G < \Delta E/2, \\ \mathcal{E}(\psi_{\lambda_3, \lambda_4}), & G > \Delta E/2, \end{cases}$$

$$E_{2^N} \simeq \mathcal{E}(\psi_{\lambda_2}).$$

By increasing the size N of the system we find that the differences between the N -body and mean-field energies indicated above increase slower than N . Assuming that these differences are $o(N)$, in Fig. 9 we compare single-particle rescaled values, namely, E_k/N , $k = 1, \dots, 2^N$, and $e_i = \mathcal{E}(\psi_{\lambda_i})/N$, $i = 1, \dots, 4$. The results shown for $N = 13$ already give an idea of what to expect for $N \rightarrow \infty$.

The diagonalization of the Hamiltonian (1) provides a full description of the excitation modes. The energy gap between the ground state and the first excited one, namely $E_2 - E_1$, is the inversion doubling, namely, the excitation of one quasimolecule from the state φ_+ to the state φ_- . For $G = 0$, the gap amounts exactly to ΔE and the excited level is N -fold degenerate. Due to the attractive dipole-dipole interaction, the value of the gap evaluated for $G > 0$ is decreased with respect to the noninteracting case by an amount of the order of G . For G large the ground state becomes twofold degenerate and the gap vanishes. In Fig. 10, we show the value of $E_2 - E_1$ evaluated as a function of G for systems of increasing size N . For any value of N the gap vanishes smoothly at $G \gg \Delta E$, however, by increasing N such smoothness becomes paler and paler. What is the behavior that we should expect in the $N \rightarrow \infty$ limit? As we will see in a moment, the mean-field indicates that $E_2 - E_1$ sharply vanishes at $G = \Delta E/2$, thus suggesting that for $N \rightarrow \infty$ a phase transition takes place.

In general, the excitation energies from the ground state can be evaluated as the poles of the Fourier transform of the linear response function [21]. In [7], we have evaluated the linear response of the mean-field Hamiltonian (2) to a time-dependent perturbation which corresponds to an electromagnetic radiation coupling with the electric dipole of

the molecules. For a gas in the mean field ψ_{λ_1} , the Fourier transform of the linear-response function is [32]

$$\mathcal{R}(\omega) = \frac{2\Delta E}{(\hbar\omega)^2 - (\Delta E^2 - 2G\Delta E)}, \quad (\text{B1})$$

which has two simple poles at angular frequency $\pm\bar{\omega}$, $\bar{\omega} = \sqrt{\Delta E^2 - 2G\Delta E}/\hbar$. We conclude that, in the region $0 \leq G < \Delta E/2$ where the gas is at equilibrium in the molecular state ψ_{λ_1} , the mean-field model predicts an inversion doubling frequency $\bar{\nu} = \bar{\omega}/(2\pi)$ given by

$$\bar{\nu} = \frac{\Delta E}{h} \sqrt{1 - \frac{2G}{\Delta E}}, \quad (\text{B2})$$

which vanishes at $G = \Delta E/2$. This behavior of $h\bar{\nu}$ is compatible with the $N \rightarrow \infty$ limit of the gap $E_2 - E_1$ which can be envisaged from Fig. 10.

APPENDIX C: PRESSURE DEPENDENCE OF NH₃ AND ND₃ INVERSION LINES: COMPARISON WITH EXPERIMENTS

In [7] we have compared the mean-field theoretical prediction for the inversion frequency with the spectroscopic data available for ammonia [9,10] and deuterated ammonia [11]. In these experiments, the central frequency of the inversion peak was measured at different pressures. The frequency is found to decrease by increasing P and vanishes for pressures greater than a critical value. This behavior is very well accounted for by the mean-field prediction (B2) for $\bar{\nu}$. In fact, an important feature of this equation is the statement that the ratio between the frequency $\bar{\nu}$ of a measured spectroscopic inversion line and the energy splitting ΔE of an isolated molecule

$$\frac{h\bar{\nu}}{\Delta E} = \sqrt{1 - \frac{P}{P_{\text{cr}}}} \quad (\text{C1})$$

is a universal function of P/P_{cr} independent of the kind of chiral species considered. In Fig. 11, we show the values of $h\bar{\nu}/\Delta E$ measured at different pressures P in the case

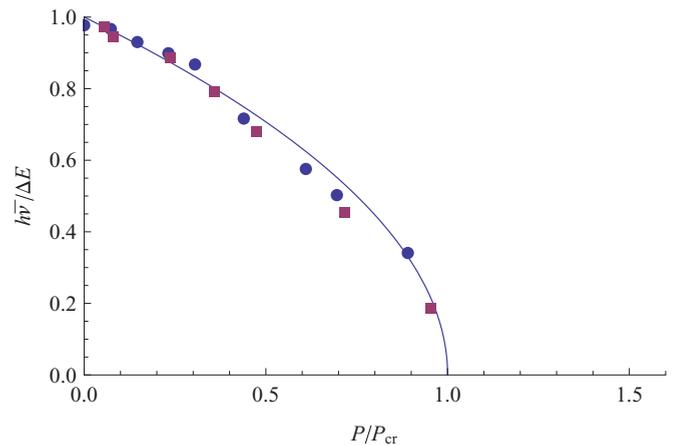


FIG. 11. (Color online) Plot of the universal function of Eq. (C1). Points are the experimental results for NH₃ (circles) or ND₃ (squares) available from Refs. [9–11], respectively. The experimental data have been scaled using the values of ΔE and P_{cr} from Table I.

of ammonia and deuterated ammonia. The superposition of the two sets of data plotted as a function of P/P_{cr} and the agreement with formula (C1) is impressive.

Some comments are in order. The mean-field prediction (C1) does not contain free parameters. The value of P_{cr} is evaluated from the electric dipole μ of the molecule, its collision diameter d and inversion energy splitting ΔE , and

the temperature T of the gas [see Eq. (4) and Table I]. We remark, however, that the experimental points shown in Fig. 11 are the result of an indirect measurement. More precisely, in experiments [9–11] the line shape of the absorption coefficient measured for NH_3 and ND_3 at different pressures P is fitted by a Van Vleck–Weisskopf formula [23] in which $\bar{\nu}$ is considered a fitting parameter.

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