Interaction Induced Localization in a Gas of Pyramidal Molecules

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We propose a model to describe a gas of pyramidal molecules interacting via dipole-dipole interactions. The interaction modifies the tunneling properties between the classical equilibrium configurations of the single molecule and, for sufficiently high pressure, the molecules become localized in these classical configurations. We explain quantitatively, without free parameters, the shift to zero frequency of the inversion line observed upon increase of the pressure in a gas of ammonia or deuterated ammonia. For sufficiently high pressures, our model suggests the existence of a superselection rule for states of different chirality in substituted derivatives.

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The behavior of gases of pyramidal molecules, i.e., molecules of the kind XY_3 such as ammonia NH_3, has been the object of investigations since the early developments of quantum mechanics [1]. However, the behavior of these systems is still debated and some experimental facts remain essentially unexplained [2].

For the single pyramidal molecule, owing to the great differences of characteristic energies and times, some adiabatic approximations hold. In particular, the one-dimensional inversion motion of the nucleus X across the plane containing the three nuclei Y can be separated from the rotational and vibrational nuclear degrees of freedom. The form of the effective potential for this motion is a double well which is symmetric with respect to the inversion plane [3]. Because of tunneling across the finite potential barrier, the eigenstates are delocalized in the two minima of the potential and, for energies below the barrier height, are grouped in doublets, i.e., couples of states with a relative splitting in energy small in comparison with the distance from the rest of the spectrum. For the pyramidal molecules under consideration, the thermal energy k_BT at room temperature is much smaller than the distance between the first and the second doublet so that the problem can be reduced to the study of a two-level system corresponding to the symmetric and antisymmetric states of the first doublet.

The existence of delocalized stationary states is clearly in disagreement with the usual chemical view which, relying upon classical theory, considers the molecules as objects with a well defined spatial structure. In particular, for the molecules under consideration the classical view predicts one of the two pyramidal configurations corresponding to the nucleus X localized in one of the wells of the inversion potential.

The quantum prediction of stationary delocalized states implies the presence of a line in the absorption spectrum, the so called inversion line, at a frequency $\bar{\nu} = \Delta E/h$, where ΔE is the energy splitting of the first doublet. Experiments performed with NH_3 [4], ND_3 [5], and NT_3 [6] reveal the existence of this inversion line in various rotational and vibrational bands. The frequency $\bar{\nu}$ of the inversion line has been measured as a function of the gas pressure P for NH_3 [7,8] and ND_3 [9]. Starting from the expected value $\Delta E/h$ at $P \simeq 0$, $\bar{\nu}(P)$ decreases by increasing P and vanishes at a critical pressure $P_{\mathrm{cr}} \simeq 1.7$ atm for NH_3 and $P_{\mathrm{cr}} \simeq 0.1$ atm for ND_3. No quantitative theory has been proposed so far for this phenomenon.

As early as 1949, in a short qualitative paper [10] Anderson made the hypothesis that dipole-dipole interaction may induce a localization of the molecular states. In this way the important idea was introduced that intermolecular interactions may be responsible for the observed phenomena. By considering a system of two or three interacting molecules, Margenau was able to predict a decrease of the inversion frequency on reducing the distance between the molecules [11]. A quantitative discussion of the collective effects induced by coupling a single molecule to the environment constituted by the other molecules of the gas was made in [12]. 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 suggests that a kind of phase transition may be invoked to explain the behavior of NH_3 and ND_3 under variation of pressure.

We have implemented this idea by constructing a simplified model of a gas of pyramidal molecules which exhibits the desired properties and allows a direct comparison with experimental data. Our model predicts, for sufficiently high intermolecular interactions, the presence of two degenerate ground states corresponding to the different localizations of the molecules. This transition to localized states gives a reasonable explanation of the experimental results [7–9]. In particular, it describes quantitatively, without free parameters, the shift to zero frequency of the inversion line of NH_3 and ND_3 on increasing the pressure.

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We model the gas as a system of molecules nearly independent in the following sense: each molecule is subjected to an external field representing the interaction with the rest of the gas to be determined self-consistently. We then analyze the linear response of this model to an electromagnetic perturbation to obtain the low energy excitation spectrum and its dependence on the intermolecular interaction. Finally, we compare our theoretical results with the available experimental data.

We mimic the inversion degree of freedom of an isolated molecule with the Hamiltonian

$$h_0 = -\frac{\Delta E}{2}\,\sigma^x, \tag{1}$$

where σ^x is the Pauli matrix in the standard representation with delocalized tunneling eigenstates

$$|1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \qquad |2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}. \tag{2}$$

Since the rotational degrees of freedom of the single pyramidal molecule are faster than the inversion ones, on the time scales of the inversion dynamics the molecules feel an effective attraction arising from the angle averaging of the dipole-dipole interaction at the temperature of the experiment [13]. In the representation chosen for the Pauli matrices, the localizing effect of the dipole-dipole interaction between two molecules i and j can be represented by an interaction term of the form $\sigma_i^z\sigma_j^z$, where σ^z has localized eigenstates

$$|L\rangle = \begin{pmatrix}1\\0\end{pmatrix} \qquad |R\rangle = \begin{pmatrix}0\\1\end{pmatrix}. \tag{3}$$

In a mean-field approximation we obtain the total Hamiltonian

$$h(\lambda) = -\frac{\Delta E}{2}\,\sigma^x - G\sigma^z\langle\lambda|\sigma^z|\lambda\rangle, \tag{4}$$

where $|\lambda\rangle$ is the single-molecule state to be determined self-consistently by solving the nonlinear eigenvalue problem associated to (4). The parameter G represents the dipole interaction energy of a single molecule with the rest of the gas. This must be identified with a sum over all possible molecular distances and all possible dipole orientations calculated with the Boltzmann factor at temperature T. If ϱ is the density of the gas, we have

$$G = \int_d^\infty \frac{\mu^4}{3(4\pi\varepsilon_0\varepsilon_r)^2 k_B T r^6}\,\varrho 4\pi r^2\,dr\,, \tag{5}$$

where ε_r is the relative dielectric constant, d is the molecular collision diameter, and the fraction in the integrand represents the Keesom energy between two classical dipoles of moment μ at distance r [13]. Equation (5) is valid in the high temperature limit which is appropriate for room temperature experiments. The exact expression, we assume ϱ is constant, is

$$G = \frac{\varrho\mu^2}{4\pi\varepsilon_0\varepsilon_r}\int_{\sqrt[3]{T/T_0}}^{\infty} dx\,4\pi x^2 \ln\left[\int_0^1 dy\int_0^1 dz\,\cosh(2yzx^{-3})\,I_0\big(\sqrt{1-y^2}\sqrt{1-z^2}\,x^{-3}\big)\right], \tag{6}$$

where $T_0 = \mu^2/(4\pi\varepsilon_0\varepsilon_r d^3 k_B)$ and $I_n(u)$ is the modified Bessel function of the first kind. Expression (6) can be evaluated numerically and the result differs very little from (5) even for $T \ll T_0$. For densities not too high, we set $\varrho = P/k_B T$ so that, at fixed temperature, the mean-field interaction constant G increases linearly with the gas pressure P. By evaluating (5) we have

$$G = \frac{4\pi}{9}\left(\frac{T_0}{T}\right)^2 P d^3. \tag{7}$$

The solution of the eigenvalue problem associated to the Hamiltonian (4) gives the following results. If $G < \Delta E/2$, there is only one ground state $|\lambda_0\rangle = |1\rangle$, with energy

$$E_0 = -\frac{\Delta E}{2}\,. \tag{8}$$

If $G \geq \Delta E/2$, there are two degenerate ground states

$$|\lambda_0^L\rangle = \sqrt{\frac{1}{2} + \frac{\Delta E}{4G}}\,|1\rangle + \sqrt{\frac{1}{2} - \frac{\Delta E}{4G}}\,|2\rangle, \tag{9}$$

$$|\lambda_0^R\rangle = \sigma^x|\lambda_0^L\rangle, \tag{10}$$

with energy

$$E_0^L = E_0^R = -\frac{\Delta E}{2} - \frac{1}{2G}\left(\frac{\Delta E}{2} - G\right)^2. \tag{11}$$

By defining the critical value $G_{\mathrm{cr}} = \Delta E/2$, we distinguish the following two cases. For $G < G_{\mathrm{cr}}$, the ground state of the system is approximated by a product of delocalized symmetric single-molecule states corresponding to the ground state of an isolated molecule. For $G \geq G_{\mathrm{cr}}$, we have two different product states which approximate the ground state of the system. The corresponding single-molecule states transform one into the other under the action of the inversion operator σ^x, see Eq. (10), and, for $G \gg G_{\mathrm{cr}}$, they become localized

$$\lim_{\Delta E/G\to 0}|\lambda_0^L\rangle = |L\rangle \qquad \lim_{\Delta E/G\to 0}|\lambda_0^R\rangle = |R\rangle. \tag{12}$$

The above results imply a bifurcation of the ground state at a critical interaction $G = G_{\mathrm{cr}}$. According to Eq. (7) and using $\varrho = P/k_B T$, this transition can be obtained by increasing the gas pressure above the critical value

$$P_{\mathrm{cr}} = \frac{9}{8\pi}\,P_0\left(\frac{T}{T_0}\right)^2, \tag{13}$$

where $P_0 = \Delta E/d^3$.

When the gas is exposed to an electromagnetic radiation of angular frequency ω_0, we add to the Hamiltonian (4) the perturbation

$$h_{\mathrm{em}}(t) = \epsilon f(t)\sigma^z, \tag{14}$$

where ϵ is a small parameter and $f(t) = \theta(t)\cos(\omega_0 t)$, $\theta(t)$ being the Heaviside function. The choice of a dipole coupling approximation, $h_{\mathrm{em}} \propto \sigma^z$, is justified for a radiation of wavelength long with respect to the molecular size. Under the effect of the perturbation (14) the single-molecule state $|\lambda(t)\rangle$ evolves according to the time-dependent nonlinear Schrödinger equation

$$i\hbar \frac{d|\lambda(t)\rangle}{dt} = [h(\lambda(t)) + \epsilon f(t)\sigma^z]|\lambda(t)\rangle, \tag{15}$$

with $h(\lambda)$ given by (4). The linear response to the perturbation (14) is expressed by the generalized susceptibility [14] $\mathcal{R}(\omega) = \tilde{S}_1(\omega)/\tilde{f}(\omega)$, where $\tilde{f}(\omega)$ and $\tilde{S}_1(\omega)$ are the Fourier transforms of $f(t)$ and $S_1(t)$, with $S_1(t)$ defined by

$$S(t) \equiv \langle\lambda(t)|\sigma^z|\lambda(t)\rangle = S_0(t) + \epsilon S_1(t) + \dots . \tag{16}$$

Let us assume that at time $t = 0$ each molecule is in the delocalized ground state $|\lambda_0\rangle = |1\rangle$. The solution of Eq. (15) with the initial condition $|\lambda(0)\rangle = |1\rangle$ gives

$$\mathcal{R}(\omega) = \frac{2\Delta E}{(\hbar\omega)^2 - (\Delta E^2 - 2G\Delta E)}. \tag{17}$$

The generalized susceptibility has a unique pole at positive frequency which corresponds to the inversion line frequency

$$\bar{\nu} = \frac{\Delta E}{h}\left(1 - \frac{2G}{\Delta E}\right)^{1/2}. \tag{18}$$

The residue of $\mathcal{R}(\omega)$ at this pole, namely, $(1 - 2G/\Delta E)^{-1/2}$, represents the corresponding transition probability.

Now we compare our theoretical analysis of the inversion line with the spectroscopic data available for ammonia [7,8] and deuterated ammonia [9]. In these experiments the absorption coefficient of a cell containing NH_3 or ND_3 gas at room temperature was measured at different pressures. The resulting data are reported in Fig. 1. The frequency $\bar{\nu}$ of the inversion line decreases by increasing P and vanishes for pressures greater than a critical value. There is a factor of about 15 between the critical pressures of NH_3 and ND_3.

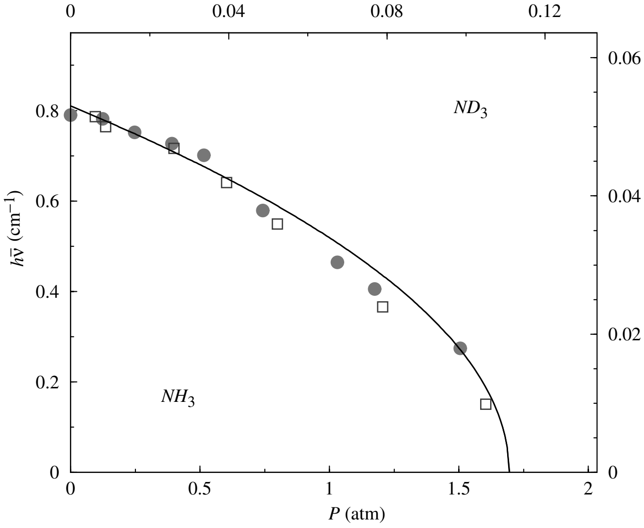

FIG. 1. Measured inversion-line frequency $\bar{\nu}$ as a function of the gas pressure P for NH_3 (dots, left and bottom scales, data from [7,8]) and ND_3 (squares, right and top scales, data from [9]). The solid line is the theoretical formula (19) with $P_{\mathrm{cr}} = 1.695$ atm for NH_3 and $P_{\mathrm{cr}} = 0.111$ atm for ND_3 calculated according to (13).

By using Eq. (7), the theoretical expression (18) for the inversion line frequency becomes

$$\bar{\nu} = \frac{\Delta E}{h}\sqrt{1 - \frac{P}{P_{\mathrm{cr}}}}, \tag{19}$$

where P_{cr} is given by (13). Note that this expression does not contain free parameters. We used the following values taken from [3,15]: $\mu = 1.47$ D, $d = 4.32$ Å, $\Delta E_{NH_3} = 0.81$ cm^{-1}, $\Delta E_{ND_3} = 0.053$ cm^{-1}. Assuming $\varepsilon_r = 1$ and $T = 300$ K, we obtain $P_{\mathrm{cr}} = 1.695$ atm for NH_3 and $P_{\mathrm{cr}} = 0.111$ atm for ND_3. The agreement of the theoretical $\bar{\nu}(P)$, also shown in Fig. 1, with the experimental data is impressive considering the simplicity of the model.

Equation (19) predicts that, up to a pressure rescaling, the same behavior of $\bar{\nu}(P)$ is obtained for different pyramidal molecules

$$\frac{\bar{\nu}_{XY_3}(P)}{\bar{\nu}_{XY_3}(0)} = \frac{\bar{\nu}_{X'Y'_3}(\gamma P)}{\bar{\nu}_{X'Y'_3}(0)}, \tag{20}$$

where $\gamma = P_{\mathrm{cr}X'Y'_3}/P_{\mathrm{cr}XY_3}$. In the case of ND_3 and NH_3, at the same temperature T we have $\gamma = \Delta E_{NH_3}/\Delta E_{ND_3} \simeq 15.28$. This factor has been used to fix the scales of Fig. 1. We see that in this way the NH_3 and ND_3 data fall on the same curve.

The intensity I of the inversion line predicted by our theoretical analysis is given, up to a constant, by the product of the photon energy $h\bar{\nu}$ and the residue of (17). The divergence of the transition probability is canceled by the vanishing photon energy and we obtain for a gas of N molecules $I \propto N\Delta E$. By writing $N = PV/k_BT$, V being the volume of the absorption cell containing the gas, we have that at fixed temperature the line intensity increases linearly with pressure. This behavior is confirmed by the experimental data [7–9].

It is interesting at this point to compare our approach with a previous study [16] where the experimental data are successfully reproduced by a formula with three free parameters for the shape factor of the inversion line. In [16] these parameters are determined by trial and error. In our work we propose a simplified theory for the shift of the inversion line based on the dipole-dipole interaction and there are no free parameters. The specific prediction of our model for the critical pressure P_{cr} in terms of the electric dipole μ of the molecule, its size d, the splitting ΔE, and the temperature T of the gas, successfully verified in the case of ammonia, should be experimentally tested also for other pyramidal gases. We emphasize that the study of the inversion spectra of pyramidal molecules, such as NH_3 and ND_3, in recent years has acquired a considerable interest in geophysical [17] and astrophysical research [18].

It is not easy to assess the region of validity of the model starting from first principles, i.e., considering all the degrees of freedom of the molecules. It is reasonable to assume that the mean-field calculation is meaningful as long as the interactions among the molecules are small compared to the inversion line frequency (18). If we take the model seriously, at least for the qualitative aspects, at pressures greater than the critical one we have the following situation. In the limit of an infinite number of molecules, the Hilbert space separates into two sectors generated by the ground state vectors given in mean-field approximation by

$$|\psi_0^L\rangle = |\lambda_0^L\rangle \cdots |\lambda_0^L\rangle, \tag{21}$$

$$|\psi_0^R\rangle = |\lambda_0^R\rangle \cdots |\lambda_0^R\rangle. \tag{22}$$

These sectors, which we call $\mathcal{H}_L$ and $\mathcal{H}_R$, cannot be connected by any operator involving a finite number of degrees of freedom (local operator). According to [2] this means that a superselection rule operates between the two sectors distinguished by the eigenvalues of an observable. It is natural [19] to define the chirality operator

$$\chi = \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} \mathbb{1}_1 \otimes \cdots \otimes \sigma_i^z \otimes \cdots \otimes \mathbb{1}_N . \tag{23}$$

It is immediately verified that

$$\langle\psi|\chi|\psi\rangle = \pm\sqrt{1 - \left(\frac{\Delta E}{2G}\right)^2} \tag{24}$$

for ψ in $\mathcal{H}_L$ and $\mathcal{H}_R$, respectively. This mean value distinguishes the two sectors but is a property weaker than ψ being an eigenstate of χ. According to (12) only in the limit $\Delta E/G \to 0$, the states ψ become completely localized and therefore eigenstates of χ. The fact that the ψ are not eigenstates of χ for $\Delta E/G \neq 0$ is connected to the nonorthogonality of the mean-field one-molecule states $|\lambda_0^L\rangle$ and $|\lambda_0^R\rangle$ and is presumably an artifact of the approximation.

This analysis has an interesting implication. Our model applies not only to molecules XY_3 but also to their substituted derivatives $XYWZ$. In fact, the difference should not matter as far as the shift of the inversion line is concerned. However, an important difference between the two cases is that for XY_3 the localized states can be obtained one from the other either by rotation or by space inversion, while for $XYWZ$ they can be connected only by space inversion. This implies that $XYWZ$ molecules at a pressure greater than the critical value are chiral and therefore optically active. Recent ultrasensitive experimental methods have been developed which allow the quantitative measurement of optical rotation in gaseous compounds [20]. It would be interesting to measure the optical activity of pyramidal gases for $P > P_{\mathrm{cr}}$.

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[1] F. Hund, Z. Phys. **43**, 805 (1927).
[2] A. S. Wightman, Nuovo Cimento Soc. Ital. Fis. **110B**, 751 (1995).
[3] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).
[4] D. M. Dennison and J. D. Hardy, Phys. Rev. **39**, 938 (1932).
[5] H. Lyons, L. J. Rueger, R. G. Nuckolls, and M. Kessler, Phys. Rev. **81**, 630 (1951).
[6] P. Helminger, F. C. De Lucia, W. Gordy, H. W. Morgan, and P. A. Staats, Phys. Rev. A **9**, 12 (1974).
[7] B. Bleaney and J. H. Loubster, Nature (London) **161**, 522 (1948).
[8] B. Bleaney and J. H. Loubster, Proc. Phys. Soc. London Sect. A **63**, 483 (1950).
[9] G. Birnbaum and A. Maryott, Phys. Rev. **92**, 270 (1953).
[10] P. W. Anderson, Phys. Rev. **75**, 1450 (1949).
[11] H. Margenau, Phys. Rev. **76**, 1423 (1949).
[12] P. Claverie and G. Jona-Lasinio, Phys. Rev. A **33**, 2245 (1986).
[13] W. H. Keesom, Phys. Z. **22**, 129 (1921).
[14] J. P. Blaizot and G. Ripka, *Quantum Theory of Finite Systems* (The MIT Press, Cambridge, MA, 1986).
[15] *CRC Handbook of Chemistry and Physics,* edited by D. R. Lide (CRC Press, New York, 1995), 76th ed.
[16] A. Ben-Reuven, Phys. Rev. Lett. **14**, 349 (1965); Phys. Rev. **145**, 7 (1966).
[17] T. R. Spilker, J. Geophys. Res. **98**, 5539 (1993).
[18] C. Henkel, R. Mauersberger, A. B. Peck, H. Falcke, and Y. Hagiwara, Astron. Astrophys. **361**, L45 (2000).
[19] G. Jona-Lasinio, C. Presilla, and C. Toninelli, in *Mathematical Physics in Mathematics and Physics: Quantum and Operator Algebraic Aspects* (American Mathematical Society, Providence, RI, 2001), Vol. 30, p. 207.
[20] T. M. Müller, K. B. Wilber, and P. H. Vaccaro, J. Phys. Chem. A **104**, 5959 (2000).