Ultracold Heteronuclear Molecules and Ferroelectric Superfluids

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(Received 13 October 2006; revised manuscript received 19 April 2007; published 13 September 2007)

We analyze the possibility of a ferroelectric transition in heteronuclear molecules consisting of Bose-Bose, Bose-Fermi, or Fermi-Fermi atom pairs. This transition is characterized by the appearance of a spontaneous electric polarization below a critical temperature. We discuss the existence of a ferroelectric Fermi liquid phase for Fermi molecules and the existence of a ferroelectric superfluid phase for Bose molecules characterized by the coexistence of ferroelectric and superfluid orders. Lastly, we propose an experiment to detect ferroelectric correlations through the observation of coherent dipole radiation pulses.

DOI: 10.1103/PhysRevLett.99.110402 PACS numbers: 05.30.−d, 03.75.Kk, 32.10.Dk, 67.90.+z

Arguably one of the next frontiers in ultracold atomic and molecular physics is the study of two-species atomic mixtures [1–6] and ultracold heteronuclear molecules composed of two-species alkali atoms such as KRb [7–9], RbCs [10], and NaCs [11]. This frontier may be advanced through the use of Feshbach resonances which have already been observed in mixtures of two-species alkali atoms [12–14] and may also become a crucial tool for tuning physical properties of heteronuclear systems.

Ultracold heteronuclear molecules made of Bose-Bose, Bose-Fermi, or Fermi-Fermi atom pairs offer many new opportunities compared to standard (Bose or Fermi) atomic systems because of their additional degrees of freedom [15–18]. For instance, when heteronuclear diatomic molecules are formed from neutral atoms, electric charge is transferred from one atom to the other leading to an electric dipole moment $|\mathbf{p}| = qR_e$, where R_e is the separation and q is the effective charge transfer between constituent atoms. These electric dipoles have equal magnitudes but random orientations at high temperatures leading to a vanishing average electric polarization. However, at low temperatures, the dipoles may all point to a particular direction producing a finite average electric polarization density $\langle \mathbf{P} \rangle$, characteristic of a ferroelectric state. In addition, when ultracold heteronuclear molecules form a Bose-Einstein condensate (BEC) a ferroelectric superfluid state proposed in this Letter may be accessible experimentally.

Our main results are as follows. When heteronuclear molecules are composite fermions (Bose-Fermi pairs), a phase transition occurs, separating a paraelectric Fermi liquid (PFL) from a ferroelectric Fermi liquid (FFL), as shown in Fig. 1(a). These phases do not exist in standard condensed matter systems, since all experimentally known ferroelectrics are very good insulators [19] and are not Fermi liquids. Furthermore, when heteronuclear molecules are composite bosons (Bose-Bose or Fermi-Fermi pairs), a ferroelectric transition with critical temperature T_{FE} may occur either above or below the BEC temperature T_{BEC}. When the molecular dipole moment and/or density are sufficiently large, then $T_{\mathrm{FE}} > T_{\mathrm{BEC}}$ leading to a paraelectric Bose liquid (PBL) for $T > T_{\mathrm{FE}}$, a ferroelectric Bose liquid (FBL) for $T_{\mathrm{FE}} > T > T_{\mathrm{BEC}}$, and to a ferroelectric BEC (FBEC) for $T < T_{\mathrm{BEC}}$, as shown in Fig. 1(b). When the molecular dipole moment and/or density are sufficiently low then $T_{\mathrm{FE}} < T_{\mathrm{BEC}}$ leading to a paraelectric Bose liquid (PBL) for $T > T_{\mathrm{BEC}}$, a paraelectric BEC for $T_{\mathrm{BEC}} > T > T_{\mathrm{FE}}$, and to a ferroelectric BEC (FBEC) for $T < T_{\mathrm{FE}}$, as shown in Fig. 1(c). The FBEC phase corresponds to a ferroelectric superfluid.

Electric dipole moment.—To describe all these phases of ultracold heteronuclear (diatomic) molecules, we consider first their internal degrees of freedom. At low temperatures, the electronic and vibrational degrees of freedom are frozen, and we can consider only molecular rotations described by the Hamiltonian $H_{\mathrm{rot}} = L^2/(M_r R_e^2)$, where $\mathbf{L}$ is the angular momentum, M_r is twice the reduced mass, and R_e is the equilibrium size of the diatomic molecule.

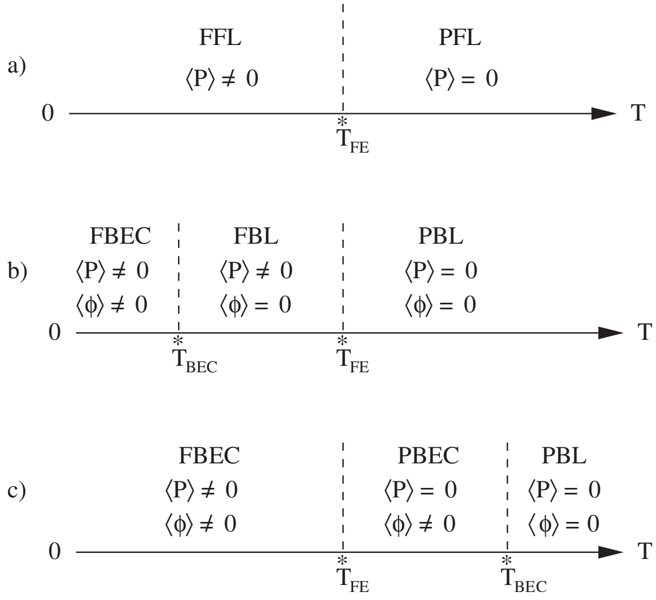

FIG. 1. Schematic phase diagram for polar (a) Fermi and (b), (c) Bose molecules, where $\langle \mathbf{P} \rangle$ and $\langle \phi \rangle$ are the corresponding order parameters for ferroelectric order at T_{FE} and for BEC at T_{BEC}, respectively.

The eigenenergies of $H_{\rm rot}$ (in units of $\hbar = 1$) are $E_\ell = \ell(\ell+1)/(M_r R_e^2)$ and the eigenfunctions are the spherical harmonics $Y_{\ell,m_\ell}(\theta,\phi)$ represented by the ket $|\ell, m_\ell\rangle$. The characteristic rotational energy is $E_{\rm rot} = E_1 - E_0 = \omega_{\rm rot}$ with frequency $\omega_{\rm rot} = 2/(M_r R_e^2)$. Since the dipole operator is $\hat{\mathbf{p}} = q\mathbf{R}_e$, then the expectation value $\langle \ell, m_\ell|\hat{\mathbf{p}}|\ell, m_\ell\rangle = 0$, for any eigenstate of $H_{\rm rot}$. However, when a static electric field is applied along the $\hat{\mathbf{z}}$ direction the states $|1,-1\rangle$ and $|1,+1\rangle$ are eigenstates of $H_E = H_{\rm rot} - \hat{p}_z E_z$, and the new ground state $|\psi_-\rangle = a|0,0\rangle + b|1,+1\rangle$ (when only states with $\ell = 0, 1$ are considered) breaks parity and produces a finite average dipole moment along the direction of the field $p_z = \langle\psi_-|\hat{p}_z|\psi_-\rangle = qR_e\{a^*b + ab^*\}/\sqrt{3}$.

Hamiltonian.—To construct a many-body Hamiltonian for ultracold molecules ($T \ll \omega_{\rm rot}$), we average over internal degrees of freedom and write the center-of-mass-only Hamiltonian density (with Einstein's sum convention)

$$H(\mathbf{r}) = \psi^*_\sigma(\mathbf{r})K(\mathbf{r})\psi_\sigma(\mathbf{r}) + H_{dd}(\mathbf{r}) + H_{ed}(\mathbf{r}), \qquad (1)$$

describing a weakly interacting gas of dilute polar molecules, where $\psi^*_\sigma(\mathbf{r})$ creates a Bose (Fermi) molecule at position $\mathbf{r}$ with pseudospin σ, and $n_\sigma(\mathbf{r}) = \psi^*_\sigma(\mathbf{r})\psi_\sigma(\mathbf{r})$ is the density operator. The first term in Eq. (1) is $K(\mathbf{r}) = -\nabla^2/(2M) - \mu + V(\mathbf{r})$, where M is the molecular mass, μ is the chemical potential, and $V(\mathbf{r})$ is the trapping potential. The second term is the density-density interaction between Bose (Fermi) molecules $H_{dd}(\mathbf{r}) = (1/2) \times \int d\mathbf{r}'[n_{\sigma'}(\mathbf{r}')U_{\sigma'\sigma}(\mathbf{r},\mathbf{r}')n_\sigma(\mathbf{r})]$ with contact interaction $U_{\sigma'\sigma}(\mathbf{r},\mathbf{r}') = U\delta(\mathbf{s})$, where $U = 4\pi a/M$ and $\delta(\mathbf{s})$ is the delta function with $\mathbf{s} = \mathbf{r} - \mathbf{r}'$. Here, a is the scattering length of the corresponding Bose (Fermi) molecules. The third term is the electric dipole-dipole interaction between molecular dipoles at positions $\mathbf{r}$ and $\mathbf{r}'$, $H_{ed}(\mathbf{r}) = -(1/2)\int d\mathbf{r}'[\mathbf{P}_\alpha(\mathbf{r}')J_{\alpha\beta}(\mathbf{r},\mathbf{r}')\mathbf{P}_\beta(\mathbf{r})]$, where the vector $\mathbf{P}(\mathbf{r}) = \mathbf{p}(\mathbf{r})\sum_\sigma n_\sigma(\mathbf{r})$ is the polarization operator, and $\mathbf{p}(\mathbf{r})$ is the molecular dipole moment at position $\mathbf{r}$. The electric dipole-dipole interaction is given by $J(\mathbf{r},\mathbf{r}') = \mathbf{p}_\alpha(\mathbf{r})J_{\alpha\beta}(\mathbf{r},\mathbf{r}')\mathbf{p}_\beta(\mathbf{r}')$, where $\{\alpha,\beta\} = \{1,2,3\}$ label the vector components, and $J_{\alpha\beta}(\mathbf{r},\mathbf{r}') = (3\mathbf{s}_\alpha\mathbf{s}_\beta/|\mathbf{s}|^2 - \delta_{\alpha,\beta})/(4\pi\varepsilon_0|\mathbf{s}|^3)$ with $\delta_{\alpha,\beta}$ being the Kronecker delta.

Electric polarization.—Within the Hartree-Fock approximation, the Hamiltonian density reduces to $H_0(\mathbf{r}) = K(\mathbf{r}) + Un_0(\mathbf{r}) - \int d\mathbf{r}'\mathbf{p}_\alpha(\mathbf{r})J_{\alpha\beta}(\mathbf{r},\mathbf{r}')\mathbf{P}_{0\beta}(\mathbf{r}')$, where the electric polarization density is $\mathbf{P}_0(\mathbf{r}) = \mathbf{p}(\mathbf{r})n_0(\mathbf{r})$, with $n_0(\mathbf{r}) = \sum_\sigma n_{0,\sigma}(\mathbf{r})$ being the local density of Bose (Fermi) molecules at $\mathbf{r}$. The average polarization $\langle\mathbf{P}\rangle = \int d\mathbf{r}\mathbf{P}_0(\mathbf{r})/V_c$ is

$$\langle\mathbf{P}\rangle = \frac{1}{V_c}\int d\mathbf{r}\mathbf{p}(\mathbf{r})\sum_{i,\sigma}|\phi_i(\mathbf{r})|^2 f_\eta(\epsilon_i), \qquad (2)$$

where V_c is the volume, $\phi_i(\mathbf{r})$ and ϵ_i are eigenfunctions and eigenvalues of $H_0(\mathbf{r})$, and $f_\eta(\epsilon_i) = 1/(e^{\beta\epsilon_i} - \eta)$ is the Bose (Fermi) distribution for Bose (Fermi) molecules when $\eta = 1\ (-1)$. The solution of Eq. (2) is nontrivial; however, analytical insight can be gained for homogenous systems where $V(\mathbf{r}) = 0$ and $\mathbf{P}_0(\mathbf{r}) = \mathbf{P}_0$ is independent of $\mathbf{r}$. We discuss the homogeneous case first and then analyze the case of a harmonic trap.

Ferroelectric critical temperature.—In the ferroelectric state, all molecular dipoles are pointing along the same direction $\hat{\mathbf{m}}$ such that $\mathbf{p}(\mathbf{r}) = \mathbf{p} = |\mathbf{p}|\hat{\mathbf{m}}$ and $\mathbf{P}_0 = |\mathbf{P}_0|\hat{\mathbf{m}}$. The critical temperature $T_{\rm FE}$ for the ferroelectric transition is found from the slope of Eq. (2) with respect to $\mathbf{P}_0$ evaluated at $\mathbf{P}_0 = 0$, leading to

$$1 + \tilde{J}(\mathbf{q}\to\mathbf{0})(\partial N/\partial\mu)_T = 0, \qquad (3)$$

from which $T_{\rm FE}$ can be calculated. Here, $\tilde{J}(\mathbf{q})$ with $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ is the Fourier transform of $J(\mathbf{s})$, and N is the number of Bose (Fermi) molecules. Using the Kac parameter γ_0 as a cutoff for short distances ($|\mathbf{s}| < 1/\gamma_0$) leads to $\tilde{J}(\mathbf{q}) = \mathbf{p}_\alpha\tilde{J}_{\alpha\beta}(\mathbf{k},\mathbf{k}')\mathbf{p}_\beta$, where $\tilde{J}_{\alpha\beta}(\mathbf{k},\mathbf{k}') = (3\mathbf{q}_\alpha\mathbf{q}_\beta/|\mathbf{q}|^2 - \delta_{\alpha,\beta})(\sin\tilde{q}/\tilde{q}^3 - \cos\tilde{q}/\tilde{q}^2)/\varepsilon_0$ with $\tilde{q} = |\mathbf{q}|/\gamma_0$. Thus, we obtain an implicit relation for the $T_{\rm FE}$

$$1 - 2|\mathbf{p}|^2\kappa(T_{\rm FE})n^2/(3\varepsilon_0) = 0, \qquad (4)$$

in terms of the molecular density $n = N/V_c$ and the isothermal compressibility $\kappa(T) = (1/n^2)(\partial n/\partial\mu)_T$.

The ferroelectric instability is accompanied by a divergence of the dielectric function in the long-wavelength and low-frequency limit. Using linear response theory, the dielectric function $\varepsilon(\mathbf{q}, iw_n)$ can be related to the density-density correlation function $C(\mathbf{q},\tau) = \langle T_\tau\hat{n}(\mathbf{q},\tau)\times\hat{n}(-\mathbf{q},0)\rangle$ and to $\tilde{J}(\mathbf{q})$ via $1/\varepsilon(\mathbf{q}, iw_n) = 1 - [\tilde{J}(\mathbf{q})/V_c]\times\int_0^{1/T} d\tau e^{iw_n\tau}C(\mathbf{q},\tau)$, where $\hat{n}(\mathbf{q},\tau)$ is the density operator. In the long-wavelength and low-frequency limit, $C(\mathbf{q},\tau)$ is directly related to $\kappa(T)$ via the compressibility sum rule [20]. Therefore, a divergent dielectric function occurs when $\varepsilon(\mathbf{q}\to 0, iw_n\to 0) = 0$ leading to $1 + \tilde{J}(\mathbf{q}\to 0)\times(\partial N/\partial\mu)_T = 0$, which is identical to Eq. (3). This relation can be applied to both Bose and Fermi systems. Next, we discuss $T_{\rm FE}$ for a weakly interacting ($a \ll \lambda$) and dilute ($na^3 \ll 1$) gas of Bose and Fermi molecules, where a is the scattering and λ is the thermal length.

Fermi molecules.—As a first application of Eq. (4), we analyze $T_{\rm FE}$ for a weakly interacting gas of Fermi molecules at any T. The molecular density is given by $n = 2F_{3/2}(z)[1 - 2F_{1/2}(z)a/\lambda_F]/\lambda_F^3$, where $\lambda_F = [2\pi/(MT)]^{1/2}$ is the thermal length and leads to $\kappa(T) \approx [F_{1/2}(z)/F_{3/2}(z) - 2F_{-1/2}(z)a/\lambda_F]/(nT)$, where $0 \le z = \exp(\beta\mu) \le \infty$ is the fugacity and $F_\nu(z) = [1/\Gamma(\nu)]\times\int_0^\infty x^{\nu-1}dx/[z^{-1}e^x + 1]$ is the Fermi integral. Here, $\Gamma(\nu)$ is the Gamma function. Thus, we obtain

$$T_{\rm FE} = \frac{2|\mathbf{p}|^2}{3\varepsilon_0}\left[\frac{F_{1/2}(z_c)}{F_{3/2}(z_c)} - \frac{2a}{\lambda_F}F_{-1/2}(z_c)\right]n, \qquad (5)$$

where $z_c = \exp(\mu/T_{\rm FE})$. Notice that, in the classical ($z_c \ll 1$) limit, Eq. (5) reduces to $T_{\rm FE} = 2|\mathbf{p}|^2(1 - 2z_c a/\lambda_F)n/(3\varepsilon_0)$, which shows that $T_{\rm FE} \propto n$ for a gas of classical electric dipoles. The $T_{\rm FE}$ for an ideal (noninteracting) gas of Fermi molecules can be obtained by setting $a = 0$. For an ideal gas, when $T_{\rm FE}$ is much smaller than the Fermi energy ϵ_F, we obtain $T_{\rm FE} \approx (2\sqrt{3}/\pi)\epsilon_F[|\mathbf{p}|^2 n/(\varepsilon_0 \epsilon_F) - 1]^{1/2}$, which is valid for $|\mathbf{p}|^2 n/(\varepsilon_0 \epsilon_F) > 1$ and $[|\mathbf{p}|^2 n/(\varepsilon_0 \epsilon_F) - 1]^{1/2} \ll 1$. For $T > T_{\rm FE}$ a PFL phase exists and for $T < T_{\rm FE}$ a FFL phase appears as shown in Fig. 1(a).

Bose molecules for $T \geq T_{\rm BEC}$.—As a second application of Eq. (4), we analyze $T_{\rm FE}$ for a weakly interacting gas of Bose molecules when $T \geq T_{\rm BEC}$. The molecular density is given by $n = B_{3/2}(z)[1 - 4B_{1/2}(z)a/\lambda_B]/\lambda_B^3$, where $\lambda_B = [1/(2\pi M T)]^{1/2}$ is the thermal length and leads to $\kappa(T) \approx [B_{1/2}(z)/B_{3/2}(z) - 4B_{-1/2}(z)a/\lambda_B]/(nT)$, where $0 \leq z = \exp(\beta\mu) \leq 1$ is the fugacity and $B_\nu(z) = [1/\Gamma(\nu)] \times \int_0^\infty x^{\nu-1}dx/[z^{-1}e^x - 1]$ is the Bose integral. Thus, we obtain

$$T_{\rm FE} = \frac{2|\mathbf{p}|^2}{3\varepsilon_0}\left[\frac{B_{1/2}(z_c)}{B_{3/2}(z_c)} - \frac{4a}{\lambda_B}B_{-1/2}(z_c)\right]n. \tag{6}$$

Notice that, in the classical ($z_c \ll 1$) limit, Eq. (6) reduces to $T_{\rm FE} = 2|\mathbf{p}|^2(1 - 4z_c a/\lambda_B)n/(3\varepsilon_0)$, which again leads to $T_{\rm FE} \propto n$ for a gas of classical electric dipoles. The $T_{\rm FE}$ for an ideal (noninteracting) gas of Bose molecules can be obtained by setting $a = 0$. Notice that the second terms in Eqs. (5) and (6) are different by a factor of 2 due to the degeneracy of pseudospin-1/2 fermions in contrast to pseudospin-0 bosons.

Bose molecules for $T \leq T_{\rm BEC}$.—As a third application of Eq. (4), we analyze $T_{\rm FE}$ for an ideal (noninteracting) gas of Bose molecules when $T \leq T_{\rm BEC}$. In this case, the molecular density is given by $n = B_{3/2}(z)/\lambda_B^3 + n_s$, where $n_s = z/[V_c(1 - z)] = \alpha(T)n$ is the density of bosons in the condensed (zero-energy) state. Here, $\alpha(T) = 1 - (T/T_{\rm BEC})^{3/2}$, where $T_{\rm BEC} = 2\pi[n/\zeta(3/2)]^{2/3}/M$ is the critical BEC temperature for noninteracting dilute bosons, and $\zeta(x)$ is the Zeta function. In this case, $\kappa(T) = [B_{1/2}(z)/\lambda_B^3 + V_c n_s^2/z]/(n^2 T)$, which diverges in the thermodynamic limit [21] when $\{N, V_c\} \to \infty$ but $n = N/V_c$ is a constant. Thus, we obtain

$$T_{\rm FE} = \frac{2|\mathbf{p}|^2}{3\varepsilon_0}\left[\frac{B_{1/2}(z_c)}{B_{3/2}(z_c)}(n - n_s) + \frac{V_c n_s^2}{z_c}\right], \tag{7}$$

which is always smaller than $T_{\rm BEC}$ and reduces to the noninteracting limit of Eq. (6) in the absence of BEC.

The two cases of Bose molecules allow the construction of the phase diagrams indicated in Fig. 1(b) and 1(c), respectively, where the PBL, FBL, PBEC, and FBEC are identified depending on the existence of a spontaneous average electric polarization $\langle \mathbf{P} \rangle$ and/or of a BEC fraction $\langle \phi \rangle$. The ferroelectric superfluid phases proposed here may be experimentally observed with currently available cooling techniques only when $T_{\rm FE}$ is large enough. This requirement imposes a condition on the size of the electric dipole moments of the molecules, and it is discussed next for the Fermi-Fermi Bose molecules.

Fermi-Fermi Bose molecules.—To set the scale, we consider the specific example of Li-K molecules consisting of ^{6}Li and ^{40}K atoms in their ground state, where $|\mathbf{p}| = 3.6$ Debye. We also choose an equal population mixture of ^{6}Li and ^{40}K atoms with parameters $N = 10^5$ and $V_c = 10^{-7}$ cm^3 leading to $T_{\rm BEC} \approx 0.099\epsilon_F$ and $T_{\rm FE} \approx 21 T_{\rm BEC}$. Here, $\epsilon_F = k_F^2/(2M_r)$ is the effective Fermi energy, where M_r is twice the reduced mass of Li and K atoms, and k_F is the effective Fermi momentum with $n = k_F^3/(6\pi^2)$. However, for a molecule with $|\mathbf{p}| = 1.0$ Debye (0.36 Debye), $T_{\rm FE} \approx 1.6 T_{\rm BEC}$ ($0.22 T_{\rm BEC}$). Heteronuclear molecules formed via Feshbach resonances or photoassociation from precooled atoms are in highly excited vibrational states, which have small $|\mathbf{p}|$. However, photoassociated RbCS molecules were brought into their vibrational ground state [22], where $|\mathbf{p}| = 1.3$ Debye, using a laser-stimulated transfer process. Furthermore, stimulated Raman adiabatic passage was used to transfer Feshbach molecules of ^{87}Rb$_2$ into lower vibrational states with high efficiency [23]. This last technique is also generalizable to heteronuclear molecules.

Therefore, it may be possible in the future to tune the dipole moment using a combination of Feshbach resonances and laser transfer processes to lower vibrational states. Depending on the values of the dipole moment, there are two cases: (i) $T_{\rm FE} > T_{\rm BEC}$ and (ii) $T_{\rm FE} < T_{\rm BEC}$. We mention in passing that as the scattering parameter $1/(k_F a)$ decreases, the size of the molecules increases and $\mathbf{p}$ gets smaller, thus producing a reduced $T_{\rm FE}$. If Li-K Feshbach molecules could be brought to lower vibrational states (or hopefully to the vibrational ground state) then they would correspond to case (i). However, other molecular systems with smaller dipole moments and/or densities may correspond to case (ii). Next, we discuss heteronuclear Bose molecules in a trap.

Heteronuclear Bose molecules in a trap.—We use a parabolic trapping potential $V(\mathbf{r}) = -\alpha|\mathbf{E}_\ell(\mathbf{r})|^2$, where α is the molecular polarizability and $|\mathbf{E}_\ell(\mathbf{r})|^2 = E_0^2 \exp[-\rho^2/(w_\rho^2) - z^2/(w_z^2)]$ is the time averaged laser intensity with $\rho^2 = x^2 + y^2$ and widths w_ρ, w_z. Thus, the trapping potential can be approximated by $V(\mathbf{r}) = V_0 + M\Omega_\rho^2\rho^2/2 + M\Omega_z^2 z^2/2$, where $V_0 = -\alpha E_0^2$ and $\Omega_i = (2\alpha E_0/M w_i^2)$ are the characteristic frequencies of the harmonic trap along $i = \rho$, z directions. When $w_z \gg w_\rho$ ($w_z \ll w_\rho$) the trap is cigar (disk) shaped.

The Thomas-Fermi approximation at $T = 0$ leads to $U n_0(\mathbf{r}) = \mu - V(\mathbf{r}) + \int d\mathbf{r}' J(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}')$, and the electric polarization density is given by $\mathbf{P}(\mathbf{r}) = \mathbf{p} n_0(\mathbf{r})$. The integral equation can be solved analytically when $\beta = [|\mathbf{p}|^2/(4\pi\varepsilon_0)]/U \ll 1$, corresponding to a small ratio between the characteristic electric dipolar energy $|\mathbf{p}|^2/(4\pi\varepsilon_0 V_c)$ and the characteristic contact interaction energy U/V_c. To zeroth order in β, the electric polarization is $\mathbf{P}(\mathbf{r}) = \mathbf{P}_{\rm TF}(\mathbf{r}) = \mathbf{p} n_{\rm TF}(\mathbf{r})$, where $n_{\rm TF}(\mathbf{r}) = n_{\rm max}[1 - \rho^2/\rho_c^2 - z^2/z_c^2]$. Here, $n_{\rm max} = (\mu - V_0)/U$, $\rho_c^2 = (\mu - V_0)/(M\Omega_\rho^2)$, and $z_c^2 = (\mu - V_0)/(M\Omega_z^2)$. The correction to first order in β for the cigar-shaped trap is

$$\delta\mathbf{P}(\mathbf{r}) = \mathbf{p}\beta\frac{4\pi}{18}\bar{n}\frac{\rho_c^2}{z_c^2}[c_1 - c_2(\rho^2/\rho_c^2 - z^2/z_c^2)], \qquad (8)$$

where c_1 and c_2 are constants, and $\bar{n} = N/V_c$. Thus, $\mathbf{P}(\mathbf{r}) = \mathbf{P}_{\mathrm{TF}}(\mathbf{r}) + \delta\mathbf{P}(\mathbf{r})$.

Possible experiment.—For the detection of ferroelectric correlations it is useful to consider time dependent nonequilibrium processes. First, consider an individual Bose molecule labeled by index "i." In this case, a π pulse of circularly polarized light propagating along the $\mathbf{z}$ axis can cause internal molecular transitions from the ground state $|\psi_-\rangle = a|0, 0\rangle + b|1, +1\rangle = |\Downarrow\rangle$ discussed in the introduction to the first excited state $|\Uparrow\rangle = |1, +1\rangle$. This amounts to inverting the Bloch vector of each molecule to the $|\Uparrow\rangle$ position. Such a state cannot radiate classically, but processes like incoherent spontaneous emission, background thermal radiations, or quantum fluctuations cause the Bloch vector to relax towards the ground state, producing a time dependent polarization vector $\mathbf{p}_i(t)$ that acts as a source for the radiation field $\mathbf{E}_i(t)$. The shape and duration of the radiation pulse requires the solution of the Maxwell-Bloch equations [24].

This single molecule description can be generalized to the many-molecule problem by considering the radiation electric field operator $\mathbf{E}(\mathbf{r}, t) = \sum_i \mathbf{E}_i(\mathbf{r}, t)$, where the field intensity is $I \sim \sum_i\langle \mathbf{E}_i \cdot \mathbf{E}_i\rangle + \sum_{i\neq j}\langle \mathbf{E}_i \cdot \mathbf{E}_j\rangle$. For a BEC where the center-of-mass kinetic energy is neglected, the Maxwell's equation for the radiation field $\mathbf{E}(\mathbf{r}, t)$ produced by a macroscopic polarization $\mathbf{P}(\mathbf{r}, t)$ is $(c^2\nabla^2 - \partial_t^2)\mathbf{E} = 4\pi\partial_t^2\mathbf{P}$, while the Bloch equation for the generalized macroscopic polarization (Bloch vector) $\mathcal{P} = (\mathcal{P}_T, \mathcal{P}_L)$ is $\partial_t\mathcal{P} = -|\mathbf{p}|\mathbf{E}_{\mathrm{eff}} \times \mathcal{P} - \mathcal{P}_T/T_2 - (\mathcal{P}_L - \mathcal{P}_L^{(0)})/T_1$, as derived from the Liouville equation for the density matrix $\mathbf{d}$. Here, T_1 (T_2) is the relaxation (dephasing) time, $\mathcal{P}_T = P_x\hat{\mathbf{x}} + P_y\hat{\mathbf{y}}$, $\mathcal{P}_L = |\mathbf{p}_T|n(\mathbf{r})(\mathbf{d}_{\Uparrow\Uparrow} - \mathbf{d}_{\Downarrow\Downarrow})\hat{\mathbf{z}}$, while $\mathbf{E}_{\mathrm{eff}} = (\mathcal{E}_T, \mathcal{E}_L)$, where $\mathcal{E}_T = (E_x + E_{\mathrm{dip},x})\hat{\mathbf{x}} + (E_y + E_{\mathrm{dip},y})\hat{\mathbf{y}}$, and $\mathcal{E}_L = -\omega_0/|\mathbf{p}_T|$, with $\omega_0 = \omega_{\mathrm{rot}} + p_z E_{\mathrm{dip},z}$. Notice that $|\mathbf{p}_T|$ is the magnitude of the transitional dipole moment between the ground and first excited state and that $\mathbf{E}_{\mathrm{dip}}$ is the dipole field due to all other molecules.

We assume that T_2 is the shortest time scale, and that after time $t = 0$ when the π pulse ends, the Bloch vector swings down monotonically to the ground state as in superradiance [25]. In our case, the radiation intensity for $T \ll \min\{T_{\mathrm{FE}}, T_{\mathrm{BEC}}\}$ is proportional to N^2:

$$I(t) \sim |\mathbf{p}|^2 N^2 \gamma \exp(-t/T_2)\mathrm{sech}^2[(t - \tau_d)/\tau_s]. \qquad (9)$$

Here, $\tau_s = 8\pi\tau_0/(N\gamma^{1/2})$ is the pulse width, τ_0 is the radiation lifetime of an isolated molecule, and $\tau_d = (\tau_s/2)\ln N$ is the delay time. Since $\mathbf{P}$ rotates primarily in the x-y plane, coherent dipole radiation is emitted mostly along $\hat{\mathbf{z}}$. In addition, $\gamma^{1/2} = \min\{N_0, N_{\mathrm{FE}}\}/N$, where N_0/N is the superfluid condensate fraction and $N_{\mathrm{FE}}/N = |\mathbf{P}|/(N|\mathbf{p}|)$ is the ferroelectric fraction. However, when $T \to T_{\mathrm{FE}}$ ($\gamma \to 0$) phase coherence between the dipoles is lost and each molecule acts as an independent emitter. In this case, the emitted radiation is essentially isotropic and proportional to the number of molecules N. Typical pulse durations for the incoherent case are $\tau_{\mathrm{inc}} \sim 1$ s for systems of two adjacent rotational levels as is the case here (see, e.g., the case of HF molecules [26]). However, in the coherent case the pulse width is much shorter by a factor of $N\gamma^{1/2}$, which for $N = 10^5$ and $\gamma = 1$ leads to $\tau_s \sim 240$ ns and $\tau_d \sim 1.38$ μs, and for $|\mathbf{p}| \sim 1.0$ Debye, $I_{\mathrm{peak}} \sim 100$ $\mu\mathrm{W/cm}^2$.

Conclusions.—We analyzed the possibility of a ferroelectric transition in Bose-Bose, Bose-Fermi, or Fermi-Fermi heteronuclear molecules. This transition is characterized by the appearance of ferroelectric order below a critical temperature. We obtained the order parameter equation, and we evaluated the transition temperature and the electric polarization for ultracold heteronuclear (Bose or Fermi) molecules. We discussed the existence of a ferroelectric Fermi liquid phase for polar Fermi molecules and the existence of a ferroelectric superfluid phase for polar Bose molecules characterized by the coexistence of ferroelectric and superfluid orders. We also proposed an experiment to detect ferroelectric correlations via the observation of coherent dipole radiation pulses.

We thank NSF (No. DMR-0304380) for support.

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