BaF molecules trapped in neon ice

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Polar molecules containing a heavy atom can greatly amplify the measurable effects of a permanent electric dipole moment of the electron (eEDM), a signature of time-reversal-violating new physics. Large ensembles of trapped polar molecules are required in order to improve the experimental limit on the eEDM and search for new physics at higher energy scales. Exploring a potential new approach to eEDM measurements, we have trapped barium monofluoride molecules in neon ice. We have mapped out a number of optical transitions and observed optical depletion of electron spin states in the trapped molecules, marking progress towards eEDM search experiments with molecules in inert ices.

The search for a permanent electric dipole moment of the electron (eEDM) offers one of the few feasible paths to studying new physics at energy scales beyond 100 TeV. Observation of a non-zero eEDM would reveal the presence of new physics that breaks time-reversal (T) symmetry, which is one of the necessary ingredients to explain the cosmic matter-antimatter asymmetry [1]. Present-day searches for the eEDM rely on measurements of electron spin precession under the influence of the large electric fields that valence electrons effectively experience in heavy polar molecules [2–3]. As with any spin precession measurement, the precision of eEDM experiments improves with increases in the spin coherence time and the number of measured molecules.

Plans for next-generation eEDM experiments involve laser cooling of gas-phase molecules to sub-millikelvin temperatures [4–6], or assembly of molecules from ultracold trapped atoms [7, 8], in order to obtain trapped molecules with long spin coherence times. But there is a simple alternative way to trap a great quantity of molecules within a small volume: freezing them within a solid [9, 10]. If the host lattice is composed of a chemically inert atom such as neon, perturbations due to the confining lattice are weak enough to allow optical state-preparation and readout of electron spins, opening up a potent approach to precision measurements [10]. Beyond the large number of molecules, the advantages of this approach are that the molecules remain fixed in both position and orientation within the lattice, yielding useful properties for controlling errors in eEDM measurements [10].

However, despite a long history of electron spin resonance experiments on matrix-isolated molecules [11, 12], high-resolution optical spectra of polar molecules in inert ices are not available. The paucity of spectroscopic data is a hindrance to the development of eEDM experiments, which rely on optical pumping to generate sizeable electron spin polarization and to precisely read out the spin precession. Therefore, laser spectroscopy of eEDM-sensitive molecules trapped in inert ices is an essential first step to unlocking the potential of these systems for precision measurements. Here we describe our observations of strong optical transitions in barium monofluoride molecules trapped in neon (BaF:Ne).

Methods. – BaF:Ne samples were grown by co-depositing BaF molecules and neon atoms onto the surface of a cooled sapphire disk. A schematic diagram of the apparatus is shown in Fig. 1.

FIG. 1: Schematic of the apparatus used for the measurements. A neon film grown on a cryogenic sapphire substrate was doped with BaF molecules produced by laser ablation in a buffer-gas cell. Fluorescence from the molecules in neon was collected using an ellipsoidal mirror and lens, and coupled to a detector outside the cryostat.

We used a pulsed Nd:YAG laser to ablate a ceramic BaF₂ disk, held within a neon buffer gas cell maintained at 20 K. A steady flow of 20 cm³/minute of neon gas was sent through the cell during the BaF:Ne sample growth process. BaF molecules produced from ablation were cooled in collisions with the neon atoms, carried by the gas flow exiting the cell and deposited 30 mm downstream onto the sapphire substrate along with the neon atoms. Absorption of a laser tuned to the gas-phase BaF X 2Σ, v = 0, J = 1/2 + → A 2Π1/2, v = 0, J = 3/2− transition was used to monitor the density of molecules in the cell (not shown in the schematic). BaF:Ne samples were typically grown at a rate of 18 µm/min for 10 minutes, after which the laser
Laser-induced fluorescence measurements were made using a tunable Ti:sapphire laser and an external-cavity diode laser. An electro-optic modulator was used to control the amplitude of the lasers and to switch it on or off rapidly (in < 10 ns). A waveplate on a motorized stage was used to control the polarization of the probe lasers. We typically used 3 mW of laser light focused onto a 30-µm-diameter spot on the neon film, although experiments were performed at a range of powers between 0.01-100 mW to ensure that the results reported here were not affected by bleaching or saturation. Laser-induced fluorescence from the illuminated region was collected using an ellipsoidal mirror and a lens, coupled out of the cryogenic vacuum system through a viewport, and sent through bandpass filters into a detector (either a spectrometer, camera or avalanche photodiode depending on the measurement). We measured the overall efficiency of our light collection to be η_c = 2 × 10⁻³ using a diffuse white scatterer placed on the substrate.

**Results.** – Dispersed fluorescence from BaF:Ne was measured on a spectrometer as the probe laser was tuned over approximately 150 nm, shown in Fig. 2. Emission between 950-1100 nm was observed following excitation of the BaF:Ne samples at a number of distinct wavelengths. Fluorescence from BaF:Ne samples remained stable and repeatable over many weeks of measurements. Fluorescence emission in the 950–970 nm band is shown plotted as a function of the wavelength of the excitation laser in Fig. 3. The spectrum reveals a clear fingerprint of BaF molecules in neon. The peaks in Fig. 3 were identified based on their close coincidence with spectral lines in gas-phase BaF molecules. The observed line centers and linewidths are listed in the Supplemental Material. Using the measured geometric and quantum efficiencies of our detection system, we estimate a fluorescence emission rate of \( \Phi_{\text{emission}} \approx 10^{13} \text{photons/s/mW} \) at the peak of the X, \( v = 0 \) → \( A^2\Pi_{1/2}, v = 0 \) resonance.

We attribute the 950–1100 nm emission features in Fig. 2 to decays from the \( A^2\Delta_{3/2} \) state to the ground electronic \( X^2\Sigma \) state, broadened by phonons due to coupling between the \( A^2 \) state and the neon lattice. We measured the dynamics of emission from the \( A^2\Delta_{3/2} \) state by monitoring fluorescence after the excitation laser was switched off. The resulting fluorescence decay curve is shown in Fig. 4. The decay is distinctly non-exponential up to 1500 ns, indicating that a simple radiative decay from the \( A^2\Delta_{3/2} \) state is not the only mechanism involved. The observed dependence of the fluorescence rate on temperature, shown in Fig. 5, is also consistent with a thermally-activated nonradiative decay pathway. We assume that a nonradiatively decaying state with lifetime \( \tau_{nr} \) and activation energy \( E_a \) competes with a radiative decay pathway that has lifetime \( \tau_r \), yielding an overall decay rate \( \tau^{-1} = \tau_r^{-1} + e^{-E_a/k_BT} \tau_{nr}^{-1} \). Then the branching ratio for radiative decay, \( \epsilon_r \), varies as

\[
\epsilon_r = \left(1 + \frac{\tau_r}{\tau_{nr}} e^{-E_a/k_BT}\right)^{-1}.
\]

This model fits well to the observed temperature dependence, with \( E_a = h\nu \times 16.2(3) \text{ cm}^{-1} \) and \( \tau_r/\tau_{nr} = 94(2) \), as shown in Fig. 5. The spatial electron distributions, bond lengths and dipole moments of the \( A^2\Delta \) states in BaF are rather different from those of the \( X^2\Sigma \) or \( A^2\Pi \) states. It is plausible that these properties are responsible for stronger coupling of the \( A^2 \) states to the neon atoms around a trapped BaF molecule, consistent with our observation that deviations from gas-phase lines were much larger for the \( A^2\Delta_{3/2} \) (≈ 58 cm⁻¹) and \( A^2\Delta_{3/2} \) states (≈ 300 cm⁻¹) states compared to the \( A^2\Pi \) states (< 7 cm⁻¹). Non-radiative quenching may also be responsible for the fact that fluorescence is predominantly emitted in the \( A^2\Delta_{3/2} \rightarrow X^2\Sigma \) band after excitation of the \( X^2\Sigma \rightarrow A^2\Pi \) transitions.

The spectrum of BaF molecules in neon presents an interesting contrast to alkali atoms in neon, where the \( s \rightarrow p \) transitions were found to be broadened and shifted (by over 100 nm in some cases) compared to the gas phase. In BaF molecules, which are isoelectronic to alkali atoms, the analogous \( X \rightarrow A \) transitions are significantly narrower and nearly unshifted from their gas-phase counterparts. This fact points to a very different local...
FIG. 3: Laser-induced fluorescence from BaF:Ne as a function of the wavelength of the excitation laser. The signal on the vertical axis is the integrated fluorescence emission between 950-970 nm, normalized by the excitation laser power at each wavelength. Note the logarithmic scale. Labels accompanying the vertical lines through the peaks denote states excited out of the ground \( X^2\Sigma, v = 0 \) state, whose corresponding gas-phase positions are indicated by bars on the horizontal axis.

FIG. 4: Time dependence of fluorescence emission, following excitation of the \( X^2\Sigma, v = 0 \rightarrow A^2\Pi_{1/2}, v = 0 \) transition at 859.4 nm. The inset shows the emission spectrum, and the shaded 950-970 nm band indicates the spectral window over which the decay time dependence was measured. The zero of time denotes the instant when the excitation laser was switched off. The decay is not consistent with a single exponential, suggesting that phonon-assisted mechanisms may be at work. The eventual exponential decay at long times (dashed line) has a \( 1/e \) time \( \tau = 1900 \) ns.

FIG. 5: Laser-induced fluorescence in the 950-970 nm band after resonant excitation of the \( X^2\Sigma, v = 0 \rightarrow A^2\Pi_{1/2}, v = 0 \) transition, as a function of the substrate temperature. The solid line is a fit to the nonradiative decay model in Eq. 1.

environment for molecules in neon ice compared to atoms. The qualitative difference between the spectra of trapped atoms and molecules has in the past been attributed to the diminished influence of the neon lattice on the valence electrons in molecules compared to atoms, since the valence electrons are partially involved in the molecular bond [18]. We posit that such an explanation cannot be
the entire story, since the valence electron in BaF occupies a non-bonding orbital that is decoupled from the Ba-F bond. Therefore, despite evidence of phonon interactions with the trapped molecules, it is remarkable that the molecular transitions shown in Fig. 3 are distinct and relatively narrow. The small spectral shifts of the $X \rightarrow A$ transitions imply that their electronic wavefunctions are not strongly perturbed by the neon lattice. The vibrational constants in the $A^2 \Pi$ states are also consistent with gas-phase values, suggesting that the Ba-F vibration is not significantly inhibited by the neighboring Ne atoms either.

The high signal-to-noise ratio of fluorescence from BaF:Ne, obtainable even with a few minutes’ worth of deposited molecules, allows us to extract some insights into the environment of the trapped molecules. For instance, the high-resolution spectrum of the $v = 0 \rightarrow A^2 \Pi_{1/2}$, $v = 0$ line in Fig. 6 shows a distinctly asymmetric lineshape. We fit this effect as a consequence of coupling between a molecule and a local phonon mode due to the change in the valence electron distribution during the optical transition. We fit the observed lineshape to the function $f(x) = \sum_{m=0}^{2} \delta(x - m \nu_p) e^{-x^2 S^m/m!}$ convolved with a gaussian with variance $\sigma^2$ centered at $\nu_0$, the frequency of the zero-phonon line. Here $S$ is the Huang-Rhys factor that parameterizes the strength of the coupling between the molecules and the mode, $\nu_p$ is the frequency of the mode and $m$ is the number of quanta in the mode. The data agree with this simple model, as shown in Fig. 6 and yields $\nu_0 = 11632.96(9) \text{ cm}^{-1}$, $\nu_p = 19.3(2) \text{ cm}^{-1}$ and $\sigma = 9.6 \text{ cm}^{-1}$. The Huang-Rhys factor, $S = \bar{m} = 0.34(1)$, implies weak coupling between the molecule and the mode. *Ab initio* calculations combined with our measurements of the coupling strength and mode frequency could identify, e.g., whether this mode represents the libration of oriented BaF molecules or their center-of-mass motion within a neon cage.

Spectroscopy of BaF:Ne also enables optical control of electron spin populations. Fig. 7 shows the dependence of fluorescence on laser polarization. The fluorescence was induced by a laser with intensity $I = 2.4 \text{ kW/cm}^2$ tuned to the $X^2 \Sigma, v = 0 \rightarrow A^2 \Pi_{1/2}, v = 0$ transition in the presence of a static magnetic field. The magnetic field was chosen such that its interaction strength with the unpaired electron in BaF ($\Omega \sim 2 \pi \times 280 \text{ MHz}$) was much stronger than the hyperfine interaction strength between the electron and $^{19}$F nuclear spin ($\delta_{\text{hf}} \sim 2 \pi \times 45 \text{ MHz}$), in order to decouple the electron spins and simplify the interpretation of measurements. The polarization of the laser was varied from linear (0°, 90°, 180°) to left (45°, $\sigma_-$) or right (135°, $\sigma_+$) circular by adjusting the angle of a quarter-waveplate. The dependence of the fluorescence on the waveplate angle was corrected for the birefringence of in-vacuum optics using the procedure described in the Supplemental Material. The decrease in fluorescence for circularly polarized laser excitation is suggestive of electron spin population transfer into dark states. This interpretation is consistent with the absence of a similar effect when the laser was tuned to the $X^2 \Sigma \rightarrow A^2 \Pi_{1/2}$ transition, where dark states are not expected to occur. Further development of this technique could enable selective optical preparation of electron spin states, which will be a useful capability for eEDM searches.

In summary, we have trapped eEDM-sensitive BaF...
molecules in neon ice and studied them using laser-induced fluorescence spectroscopy. We have identified strong optical transitions and used them to discern details of the trapping environment of the molecules. We have also used the transitions identified in this work to optically manipulate the spins of trapped molecules. We anticipate that our observations will enable further investigations into the rich physics of trapped molecules in inert ices, and spark the development of novel precision searches for new physics.

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SUPPLEMENTAL MATERIAL

A. Line centers and widths

| transition | wavelength (nm) | wavenumber (cm$^{-1}$) | FWHM (cm$^{-1}$) | shift (cm$^{-1}$) |
|------------|----------------|-------------------------|-----------------|-----------------|
| $X, v = 0 \rightarrow A^2 \Pi_{3/2}, v = 1$ | 787.66(5) | 12692.3(8) | 25.2(19) | -6.2(8) |
| $X, v = 0 \rightarrow A^2 \Pi_{3/2}, v = 0$ | 815.572(2) | 12257.973(8) | 28.60(8) | -3.88(3) |
| $X, v = 0 \rightarrow A^2 \Pi_{1/2}, v = 1$ | 828.302(6) | 12069.57(9) | 24.3(2) | 4.12(9) |
| $X, v = 0 \rightarrow A^2 \Pi_{1/2}, v = 0$ | 859.385(3) | 11633.03(5) | 23.15(9) | 3.08(5) |
| $X, v = 0 \rightarrow A'^2 \Delta_{5/2}, v = 1$ | 868.52(6) | 11510.6(8) | 18.3(15) | -58.0(8) |
| $X, v = 0 \rightarrow A'^2 \Delta_{5/2}, v = 0$ | 902.73(4) | 11074.4(4) | 22.8(9) | -55.3(4) |
| $X, v = 0 \rightarrow A'^2 \Delta_{3/2}, v = 1$ | 920.9(7) | 10856(8) | 84(23) | -298(8) |

TABLE I: Center wavelengths (in air), center wavenumbers (in vacuum), and full-widths at half maximum for the observed transitions in BaF:Ne. The last column lists the difference between the observed lines and the corresponding gas-phase BaF transitions.

B. Birefringence correction

To obtain the data shown in Fig. 7, we used two waveplates to sample uniformly over all possible polarization states of the excitation beam. Fig. 8 shows the fluorescence rate as a function of polarization state, visualized over the surface of the Poincaré sphere. There are two antipodal minima in fluorescence rate, corresponding to pure circular polarization at the location of BaF:Ne sample. A small amount of birefringence in the in-vacuum optics tilts these points away from the vertical axis.

![FIG. 8: Fluorescence rate as a function of polarization state, visualized over the surface of the Poincaré sphere. The two antipodal minima in fluorescence are tilted with respect to the vertical due to residual birefringence of in-vacuum optics.](image)

After correcting for this tilt, we average the fluorescence rate azimuthally over the Poincaré sphere. This eliminates the effect of the angular distribution of emitted fluorescence for the following reason. The emission pattern from a classical dielectric scatterer follows the angular distribution

$$I_{CP}(\theta, \phi) \propto \frac{1}{2} (1 + \cos^2 \theta)$$
when illuminated with circularly polarized light propagating along the $z$-axis, and

$$I_x(\theta, \phi) \propto \sin^2 \theta \sin^2 \phi + \cos^2 \theta$$

when illuminated with $x$-polarized light. Here $\theta, \phi$ are the polar and azimuthal angles, respectively, in a $z$-aligned spherical coordinate system. Thus the efficiency of the fluorescence collection optics will vary depending on the incident light polarization. However, observe that

$$\int_0^{2\pi} I_{CP}(\theta, \phi) \, d\phi = \int_0^{2\pi} I_x(\theta, \phi) \, d\phi,$$

so performing an azimuthal average over the Poincaré sphere eliminates the polarization dependence. After this procedure, any variations in the averaged signal are due to changes in the total emission rate as a function of polarization.