



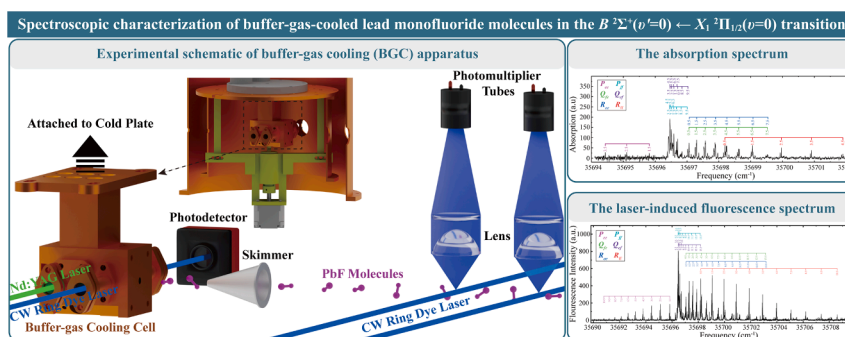
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Spectrochimica Acta Part A:
Molecular and Biomolecular Spectroscopyjournal homepage: www.journals.elsevier.com/spectrochimica-acta-part-a-molecular-and-biomolecular-spectroscopySpectroscopic characterization of buffer-gas-cooled lead monofluoride molecules in the $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ transitionZesen Wang^a, Renjun Pang^a, Jie Ma^a, Qinning Lin^a, Shunyong Hou^a, Hailing Wang^a, Xiaohu Li^{b,g,h}, Liang Xu^e, Xingjia Li^f, Guanglong Chen^f, Jinjun Liu^{d,*}, Jianping Yin^a, Tao Yang^{a,b,c,**}^a State Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062, PR China^b Xinjiang Astronomical Observatory, Chinese Academy of Sciences, 150 Science 1 – Street, Urumqi, Xinjiang 830011, PR China^c Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, PR China^d Department of Chemistry and Department of Physics, University of Louisville, Louisville, KY 40292, USA^e Shanghai Key Lab of Modern Optical System, University of Shanghai for Science and Technology, Shanghai 200093, PR China^f School of Mathematics, Physics and Statistics, Shanghai University of Engineering Science, Shanghai 201620, PR China^g Xinjiang Key Laboratory of Radio Astrophysics, 150 Science 1-Street, Urumqi, Xinjiang 830011, PR China^h Key Laboratory of Radio Astronomy and Technology, Chinese Academy of Sciences, A20 Datun Road, Chaoyang District, Beijing, 100101, PR China

HIGHLIGHTS

- We demonstrated the buffer-gas cooling production of the lead monofluoride (PbF) beam and observed the $B(v'=0) \leftarrow X_1(v=0)$ transition.
- We identified 171 hyperfine-structure-resolved transitions for three PbF isotopologues and reported hyperfine constants owing to both ^{207}Pb and ^{19}F nuclei.
- The buffer-gas-cooled PbF beam and its spectroscopic characterization will be essential in developing sensitive detection schemes for measuring the electron Electric Dipole Moment (eEDM).

GRAPHICAL ABSTRACT



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ABSTRACT

Establishing a nonzero measurement of the electron Electric Dipole Moment (eEDM) has long been a fundamental pursuit in atomic, molecular and optical physics, offering possible insights into new physics beyond the Standard Model. In this regard, lead monofluoride (PbF) has emerged as a potential candidate for measuring eEDM primarily due to its suitable properties such as the strong internal effective electric field, and eEDM-sensitive ground state with large Ω -doubling and small magnetic g factor. In the present work, we realized the production of a buffer-gas-cooled PbF molecular beam and characterized its high-resolution spectroscopy in the $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ transition, including both direct absorption and laser-induced fluorescence spectroscopy. A highly concentrated beam of PbF molecules is obtained with a central forward velocity of 223 ± 17 m/s, while

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81, 66 and 24 hyperfine-structure-resolved spectral lines with a frequency accuracy of 40 MHz have been assigned respectively for ^{208}PbF , ^{207}PbF and ^{206}PbF isotopologues. The hyperfine constants due to the ^{19}F nucleus ($A_{\parallel}$ and $A_{\perp}$) of the B state are reported for the first time, and those of the ^{207}Pb nucleus have been also updated. Such a cryogenic molecular beam of PbF in association with its hyperfine-structure-resolved spectral atlas of the $B\ ^2\Sigma^+(v'=0) \leftarrow X_1\ ^2\Pi_{1/2}(v=0)$ transition will be essential in developing sensitive detection schemes towards the $e\text{EDM}$ measurement.

1. Introduction

The electron Electric Dipole Moment ($e\text{EDM}$) could arise due to the simultaneous violation of Parity (P) and Time-reversal (T) symmetries, rendering a nonzero $e\text{EDM}$ indicative of new physics beyond the Standard Model [1–6]. For the last few decades, many experiments have been conducted to establish a series of more stringent new upper bounds on $e\text{EDM}$ [7–21]. At present, heavy polar diatomic molecules have been demonstrated to provide the smallest upper bounds on the $e\text{EDM}$, with a HfF^+ source yielding the best result of $|d_e| < 4.1 \times 10^{-30} \text{ e}\cdot\text{cm}$ [19,21], followed by ThO [17,20] and YbF [14]. Other diatomic or even polyatomic molecules, such as WC [22], RaF [23], ThF^+ [24], HgH [25], BaF [26], RaH [27], HgF [28], CdH [29], SrOH [30], and YbOH [31] have also been proposed. In comparison, the lead monofluoride (PbF) molecule possesses a relatively large molecular dipole moment, strong internal effective electric field [32,33], and $e\text{EDM}$ -sensitive ground state with large Ω -doubling and small magnetic g factor [34], thus making it another promising candidate for the $e\text{EDM}$ measurement [34,35].

Cryogenic buffer-gas cooling (BGC) has been extensively adopted as a powerful technique to produce cold and slow molecular beams [36] for applications in precision spectroscopy [37–40], cold collisions [41–45], laser cooling [31,46–49], magneto-optical traps [50–53], and Bose-Einstein condensation [54]. In the $e\text{EDM}$ measurement, the molecular beam of interest is typically cool and slow to increase the coherence time of the laser-molecule interaction. Previously by utilizing the BGC technique [14], a YbF molecular beam was cooled to below 100 μK , which increases the coherence time from 0.642 ms to 150 ms. In the ACME II project employing the metastable ThO molecule, a coherence time of about 1 ms was achieved with a forward velocity of 200 m/s using BGC [20]. PbF molecules adopted in the spectroscopic measurement so far have not been realized in a BGC setup but in either a thermal reactor or a supersonic jet expansion. In the thermal reactor experiment, PbF molecules were produced at high temperatures of 300–700 K or 1100–1200 K in a chemical reaction between either Pb and F_2 [55–59] or Pb and MgF_2 [60–63]. In a supersonic jet expansion setup, the PbF beam was obtained by ablating Pb target with a pulsed Nd:YAG laser followed by reactions with SF_6 [64]. However, the former source depicted a pronounced ground-state rotational distribution in much higher J ground levels while the latter one produced a beam with forward velocity greater than 1000 m/s, none of which is suitable for precision measurement and cold chemistry.

The spectroscopic characterization of PbF molecules has been investigated in order to choose appropriate state-selective detection schemes for the $e\text{EDM}$ experiment. Previously, Shafer-Ray *et al.* achieved PbF detection in a supersonic molecular beam using the resonance-enhanced multiphoton ionization (REMPI) technique, with either $A\ ^2\Sigma^+$ or $B\ ^2\Sigma^+$ state as the intermediate state for ionization [60,65]. Although REMPI technique offers comparable or even higher sensitivity than direct absorption or laser-induced fluorescence (LIF) spectroscopy, the latter two are non-intrusive detection techniques and allow for optimizing the production yield of cryogenic PbF molecules *in situ*. Also, single-mode continuous-wave (CW) lasers can be used as light sources for absorption and LIF detections, enabling narrower spectral linewidths and high signal-to-noise ratio simultaneously. This is particularly beneficial for the detection of the $A\ ^2\Sigma^+$ state that has a lifetime of 5 μs [66], corresponding to a natural linewidth of 32 kHz. In addition, total and dispersed fluorescence measurements can provide valuable

information for the preparation of ground-state populations of single quantum levels using the stimulated Raman adiabatic passage (STIRAP) technique.

In this article, we demonstrate the production of the buffer-gas-cooled PbF molecules via the reaction of laser-ablated Pb with the carbon tetrafluoride (CF_4) gas in the helium (He) carrier gas, which is characterized by both direct absorption and LIF spectroscopy in the $B\ ^2\Sigma^+(v'=0) \leftarrow X_1\ ^2\Pi_{1/2}(v=0)$ transition. The forward beam velocity is determined to be $223 \pm 17 \text{ m/s}$ by collecting fluorescence signal at two downstream spots, while hyperfine-structure-resolved spectra for ^{208}PbF , ^{207}PbF and ^{206}PbF have been obtained and assigned with an accuracy of 40 MHz. In contrast to the $B\ ^2\Sigma^+$ state characterization by LIF detection in our supersonic jet expansion experiment [64], we manage to resolve the hyperfine splitting due to the fluorine (^{19}F) nucleus limited by residual Doppler broadening, which have also been clearly distinguished by theoretical calculations. We are then able to update the molecular constants for the $B\ ^2\Sigma^+(v'=0)$ state of PbF , and present the improved hyperfine constant b and dipole–dipole interaction constant c for low- J levels of the B state. Our spectroscopic work here not only provides a spectral atlas of cryogenic PbF molecules in the $B\ ^2\Sigma^+(v'=0) \leftarrow X_1\ ^2\Pi_{1/2}(v=0)$ transition with better resolution and updated molecular constants, but offers an alternative molecular candidate that can be employed to measure $e\text{EDM}$ in the spirit of the Ramsey beam resonance technique as well [67].

2. Experimental setup

The absorption and laser-induced fluorescence spectra of the $B\ ^2\Sigma^+(v'=0) \leftarrow X_1\ ^2\Pi_{1/2}(v=0)$ transition of PbF were collected at the State Key Laboratory of Precision Spectroscopy, East China Normal University. The cryogenic BGC cell is attached to the cold plate of a two-stage closed-cycle He pulse tube cryocooler (Cryomech PT415) in the source chamber at a pressure of $2 \times 10^{-6} \text{ Pa}$, heat-shielded by two layers of gold-plated copper cylinders coated with activated charcoals, and is stabilized to a temperature of $5.5 \pm 0.2 \text{ K}$ (Fig. 1). PbF molecules are generated in the cell by the reaction of Pb plasma seeded in the He carrier gas with a flow rate of 2 sccm and CF_4 gas of 0.2 sccm, the former of which is created by ablating a rotating Pb rod via using second harmonic generation of a Continuum Surelite II (Model SLII-10) Nd:YAG laser system (532 nm, 2 Hz repetition rate, pulse energy 25 mJ). Laser output from continuous-wave (CW) ring dye lasers (Sirah, Matisse DS) is frequency-doubled to $\sim 280 \text{ nm}$ and set to approximately 20 mW/cm^2 in order to probe the $B\ ^2\Sigma^+(v'=0) \leftarrow X_1\ ^2\Pi_{1/2}(v=0)$ transition of PbF in the range between 35689.9 cm^{-1} and 35709.7 cm^{-1} . The fundamental frequency of the laser is monitored using a HighFinesse WSU-30 wave-meter with an absolute frequency accuracy of 30 MHz. The absorption laser beam interacts with PbF molecules 15 mm downstream from the ablation spot and is then probed by a photodetector (Thorlabs PDA25K2). The absorption signal intensity (I_{abs}) is normalized in terms of the absorption fraction $c = 1 - I_{\text{abs}}/I_{\text{avg}}$, where I_{avg} is the mean value of the background level signal [68]. The LIF spectra are simultaneously collected at two spots where the excitation laser beam ($\sim 280 \text{ nm}$) intercepts the PbF molecules at 343 mm and 406 mm downstream from the ablation source. The fluorescence signals at these two spots are individually collected via a lens system composed of an aspherical lens of 16 mm focal length and a plano-convex spherical lens of 100 mm focal length in order to maximize the collection solid angle, prior to entering

each photomultiplier tube (Hamamatsu H3695-10). The absorption and fluorescence signals are eventually transmitted to the data acquisition card (NI PCI-5122) synchronized to the Q-switch timing of the Nd:YAG laser.

3. Spectral results and analysis

Fig. 2 illustrates the PbF absorption spectrum of the $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ transition in the BGC cell. Rotational branches of ^{208}PbF are labeled by $P_{ee}(J)$, $P_{ff}(J)$, $Q_{fe}(J)$, $Q_{ef}(J)$, $R_{ee}(J)$ or $R_{ff}(J)$. Here P , Q and R indicate $J' = J - 1$, J and $J + 1$ transitions, while J' and J are quantum numbers of the total angular momentum excluding the nuclear spin for the B and X_1 states, respectively. The first and second “ e/f ” subscripts are the conventional labeling of the J -dependent parity of ro-vibronic wavefunctions for the upper and lower energy levels. For an $S = 1/2$ state (S is the total electron spin), the “ e/f ” parity is determined by the sign of the product $q\chi = p_s(-1)^{J-1/2}$, where $p_s = \pm 1$ is the parity with respect to all coordinates excluding the nuclear spin [62,69,70]. The preliminary fitting of the absorption spectrum is obtained by the incorporating $X_1(v=0)$ and $B(v'=0)$ energy level structures [56,63], and six rotational branches of the ^{208}PbF isotopologue have been further identified (Fig. 2). We have also observed the absorption spectra of ^{206}PbF and ^{207}PbF , which are intertwined with those of ^{208}PbF and prohibit us from identifying hyperfine-structure-resolved transitions due to Doppler broadening [39,68,71].

Fig. 3(a) illustrates the LIF spectrum of the $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ transition obtained in the range between 35689.9 and 35709.7 cm^{-1} . In order to assign the partially-resolved hyperfine structures, we adopt the multi-peak least-squares fitting to determine central frequency of each individual line. As indicated in Fig. 3(b), the hyperfine manifold in ^{208}PbF ($J = 3.5$) can be assigned to $B(J' = 3.5, f, F_1' = 4) \leftarrow X_1(J = 3.5, e, F_1 = 4)$, $B(J' = 3.5, f, F_1' = 3) \leftarrow X_1(J = 3.5, e, F_1 = 3)$, $B(J' = 4.5, e, F_1' = 5) \leftarrow X_1(J = 3.5, e, F_1 = 4)$ and $B(J' = 4.5, e, F_1' = 4) \leftarrow X_1(J = 3.5, e, F_1 = 3)$ transitions, denoted as $Q_{fe,4-4}(3.5)$, $Q_{fe,3-3}(3.5)$, $R_{ee,5-4}(3.5)$ and $R_{ee,4-3}(3.5)$, respectively. In Fig. 3(c), we measured two fluorescence profiles of the $Q_{ef}(0.5)$ transition at 35696.7054 cm^{-1} simultaneously, which were recorded at 343 mm and 406 mm separately downstream from the ablation spot. The forward velocity of the PbF molecular beam can therefore be derived from $v = \Delta L / \Delta t$ [72], where ΔL is the distance between the two LIF detection spots, and Δt is the time interval between the peaks of two profiles. This relation is accurate since molecules travel at a distance significantly greater than the cell's length. To ensure a relatively strong fluorescence signal, we maintained the He and CF_4 flow rates at 2 sccm and 0.2 sccm, and set the ablation laser pulse energy to be

15.6 mJ. Under these experimental conditions, the average forward velocity of PbF molecules is determined to be 223 ± 17 m/s, which is close to previously-reported velocities of other buffer-gas-cooled molecular beams such as SrF [73] and BaF [74].

It shall be noticed that the LIF spectrum exhibits both broader spectral range and better resolved transition lines than the absorption spectrum. The average linewidth in the LIF spectrum is estimated to be 120 MHz, leading to a rotational temperature of 5.6 K [39], which makes the assignment of hyperfine transitions in the LIF spectrum more accessible than that in the absorption spectrum. On the other hand, the rotational temperature of the molecular beam was determined to be about 5 K by reproducing the relative transition intensities of the LIF spectrum [68]. The proximity of these two temperatures indicates that the molecular beam is highly concentrated in the LIF detection region, ensuring sufficient PbF molecules when reaching the detection region of the eEDM measurement.

The fluorescence intensity at the 343-mm spot is about four times stronger than that at the 406-mm spot when both LIF excitation laser beams are introduced. However, the latter one will increase to the same magnitude if we block the excitation laser beam at the 343-mm spot (Fig. 3(c)). This phenomenon implies that we produce a cryogenic molecular beam of good convergence, and can be well explained by the population decay to intermediate states following the laser excitation. The radiative lifetimes of the intermediate $A^2\Sigma^+(v=0, 1)$ and $X_2^2\Pi_{3/2}(v=0)$ states are $\tau_A(v=0, 1) = 5.0 \pm 0.3 \mu\text{s}$ [66] and $\tau_{X_2}(v=0) = 370 \pm 40 \mu\text{s}$ [58]. In addition, vibrational and rotational levels of the X_1 state can host the population that decays from the B state. Therefore, the intensity difference between the LIF signals of two downstream spots is attributed to that, only a small fraction of molecules excited from X_1 to B at the 343-mm spot decays back to the original ground levels when PbF molecules arrive at the 406-mm spot after the flight time of 283 μs .

We now focus on the interpretation of the LIF spectrum of PbF molecules, in which 81, 66, and 24 hyperfine-structure-resolved spectral lines of ^{208}PbF , ^{207}PbF , and ^{206}PbF from 35689.9 to 35709.7 cm^{-1} have been identified and further assigned. The hyperfine-structure-resolved rotational distribution of the ^{208}PbF isotopologue is indicated in Fig. 3(a), while all observed transitions along with their residuals between observed and calculated frequencies, are compiled in Tables 1 and 2. We designate these lines of the $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ transition in a similar way described in Ref. [62]. Transitions of ^{206}PbF and ^{208}PbF isotopologues, which have net zero nuclear spin from Pb, are denoted as $\Delta J_{q'\chi'q\chi, F_1'-F_1}(J)$. Here O , P , Q , R and S indicate $\Delta J = J' - J = -2, -1, 0, 1$ and 2 , respectively. The subscript $q'\chi'$ or $q\chi$ is the J -dependent parity as described before, while F_1' or F_1 represents the B -state or X_1 -state total

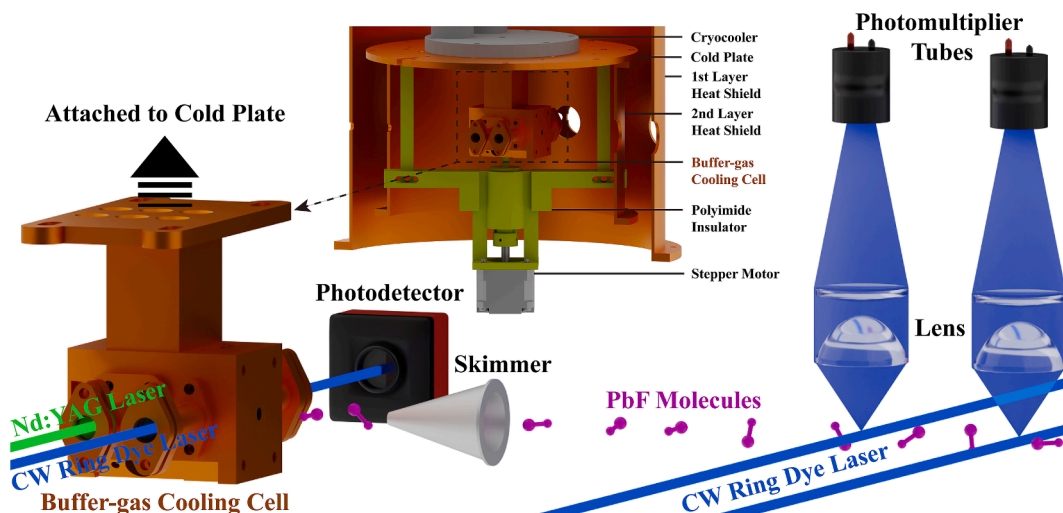


Fig. 1. Experimental schematic of buffer-gas cooling (BGC) apparatus for the measurement of the direct absorption and LIF spectroscopy of PbF molecules.

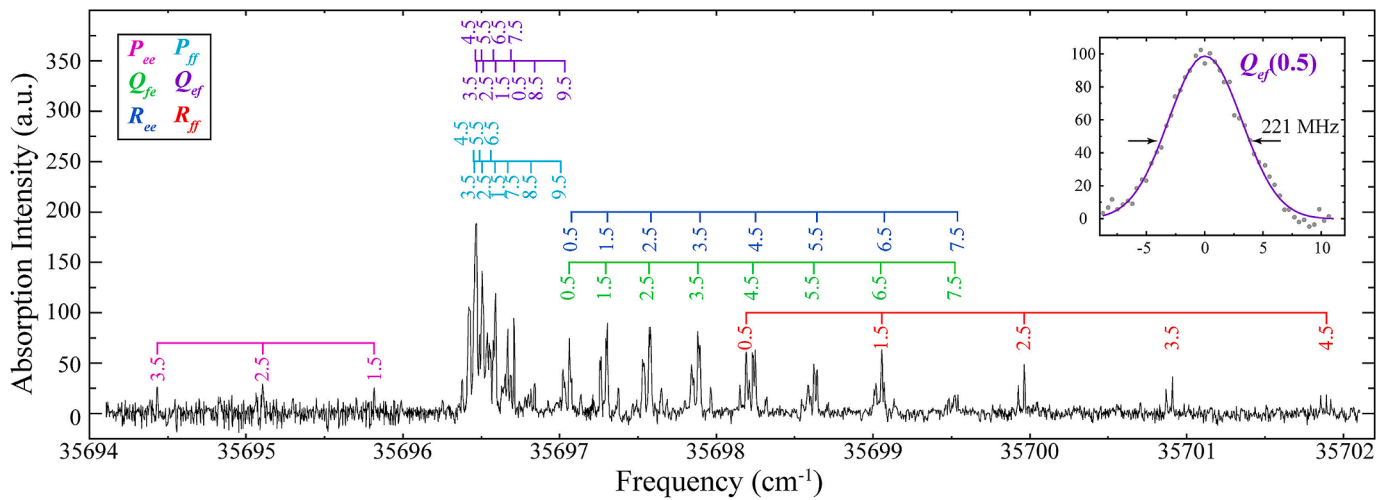


Fig. 2. The absorption spectrum of the $B\ 2\Sigma^+(v'=0) \leftarrow X_1\ 2\Pi_{1/2}(v=0)$ transition of PbF in the BGC cell. Ground-state J values of different rotational branches of ^{208}PbF are labeled in color. The inset exemplifies the $Q_{ef}(0.5)$ transition at $35696.70913(5)\text{ cm}^{-1}$, which is fitted in a Gaussian profile with the full width at half maximum (FWHM) of 221 MHz.

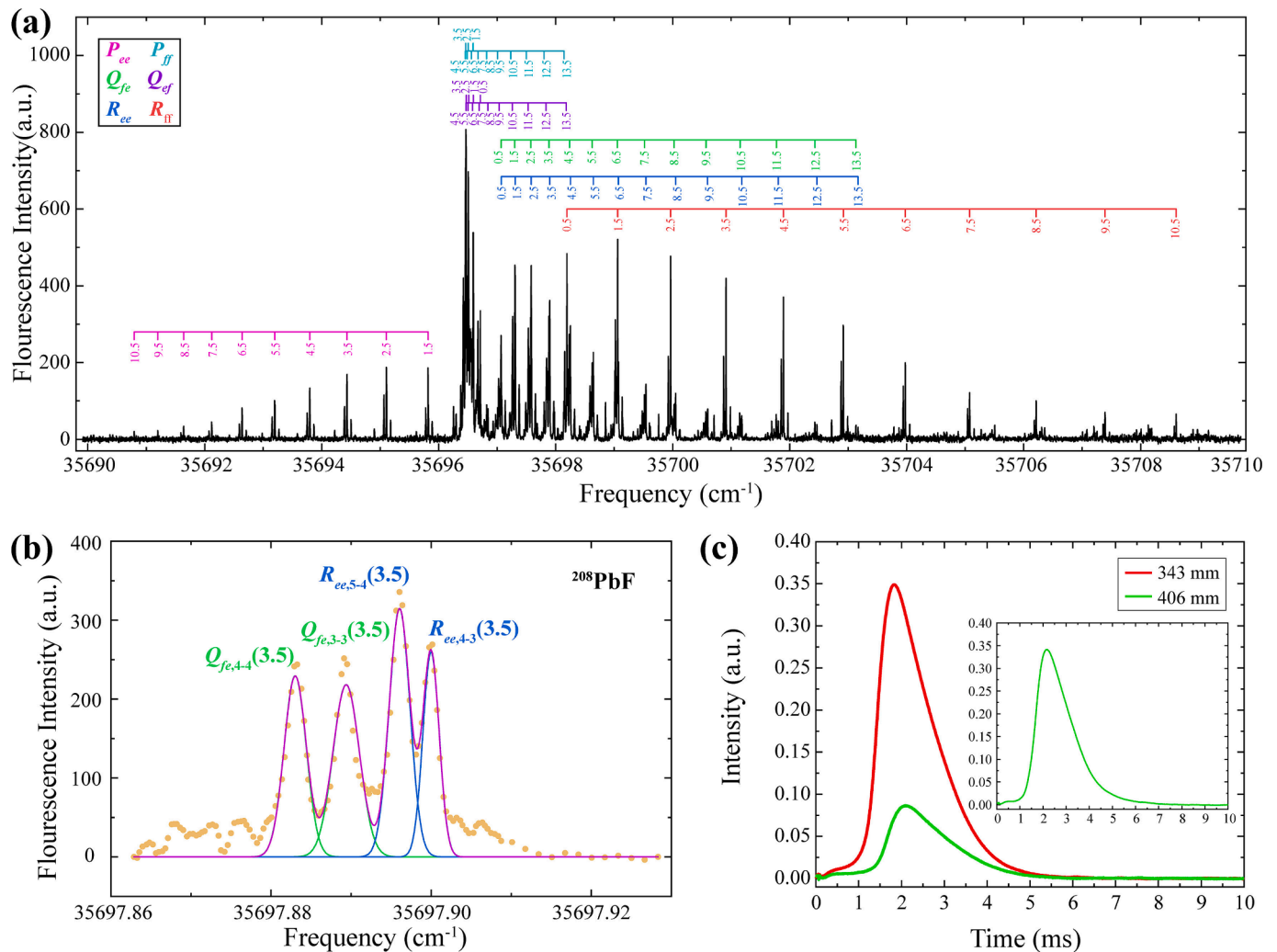


Fig. 3. (a) The laser-induced fluorescence (LIF) spectrum of the $B\ 2\Sigma^+(v'=0) \leftarrow X_1\ 2\Pi_{1/2}(v=0)$ transition of PbF. Ground-state J values of different rotational branches of ^{208}PbF are labeled in color. (b) The experimental hyperfine manifold in ^{208}PbF ($J=3.5$) (dotted) and its assignment using the multi-peak least-squares fitting method (solid). (c) The fluorescence profiles of the $Q_{ef}(0.5)$ transition recorded at 343 mm and 406 mm downstream from the ablation spot separately. The fluorescence profile in the inset indicates the signal at the 406-mm spot when no LIF excitation laser at the 343-mm spot is introduced.

Table 1

The hyperfine-structure-resolved transitions in $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ of ^{208}PbF by LIF spectroscopy. The residuals between observed and calculated transition frequencies are presented in the parentheses of observed frequency values (Obs.).

Label	Obs. (cm ⁻¹)	Label	Obs. (cm ⁻¹)	Label	Obs. (cm ⁻¹)
$P_{ee,12-13}(12.5)$	35690.09850(−46)	$P_{ff,7-8}(8.5)$	35696.81664(−51)	$R_{ee,7-6}(5.5)$	35698.64045(−39)
$P_{ee,11-12}(12.5)$	35690.10226(−28)	$P_{ff,8-9}(8.5)$	35696.82040(27)	$R_{ee,6-5}(5.5)$	35698.64426(−48)
$P_{ee,8-9}(8.5)$	35691.63731(20)	$Q_{ef,8-8}(8.5)$	35696.83875(2)	$R_{ee,8-7}(6.5)$	35699.07149(4)
$P_{ee,7-8}(8.5)$	35691.64109(28)	$Q_{ef,9-9}(8.5)$	35696.84449(89)	$R_{ee,7-6}(6.5)$	35699.07586(59)
$P_{ee,7-8}(7.5)$	35692.11833(−4)	$P_{ff,8-9}(9.5)$	35697.00396(−73)	$Q_{fe,8-8}(7.5)$	35699.51742(22)
$P_{ee,6-7}(7.5)$	35692.12264(52)	$P_{ff,9-10}(9.5)$	35697.00704(−66)	$Q_{fe,7-7}(7.5)$	35699.52308(24)
$P_{ee,6-7}(6.5)$	35692.63760(−71)	$Q_{fe,1-1}(0.5)$	35697.06105(−61)	$R_{ee,9-8}(7.5)$	35699.53976(−92)
$P_{ee,5-6}(6.5)$	35692.64156(−56)	$Q_{fe,0-1}(0.5)$	35697.06229(29)	$R_{ee,8-7}(7.5)$	35699.54443(0)
$P_{ee,5-6}(5.5)$	35693.19593(−98)	$R_{ee,2-1}(0.5)$	35697.06631(−58)	$R_{ff,3-2}(2.5)$	35699.96360(−11)
$P_{ee,4-5}(5.5)$	35693.20013(−69)	$Q_{fe,1-0}(0.5)$	35697.07099(−92)	$R_{ff,4-3}(2.5)$	35699.96635(30)
$P_{ee,4-5}(4.5)$	35693.79466(47)	$R_{ee,1-0}(0.5)$	35697.07520(−100)	$Q_{fe,9-9}(8.5)$	35700.02262(22)
$P_{ee,3-4}(4.5)$	35693.79908(85)	$Q_{fe,2-2}(1.5)$	35697.29688(12)	$Q_{fe,8-8}(8.5)$	35700.02848(50)
$P_{ee,3-4}(3.5)$	35694.43106(94)	$R_{ee,2-1}(1.5)$	35697.30933(−58)	$Q_{fe,10-10}(9.5)$	35700.56646(25)
$P_{ee,2-3}(3.5)$	35694.43504(68)	$Q_{fe,3-3}(2.5)$	35697.57043(9)	$Q_{fe,9-9}(9.5)$	35700.57256(81)
$P_{ee,2-3}(2.5)$	35695.10534(63)	$Q_{fe,2-2}(2.5)$	35697.57679(5)	$R_{ee,11-10}(9.5)$	35700.59586(91)
$P_{ee,1-2}(2.5)$	35695.11045(114)	$R_{ee,4-3}(2.5)$	35697.58072(4)	$R_{ee,10-9}(9.5)$	35700.59878(17)
$P_{ee,1-2}(1.5)$	35695.81829(32)	$R_{ee,3-2}(2.5)$	35697.58496(−31)	$R_{ff,4-3}(3.5)$	35700.90893(31)
$P_{ee,0-1}(1.5)$	35695.82188(50)	$Q_{fe,4-4}(3.5)$	35697.88310(60)	$R_{ff,5-4}(3.5)$	35700.91183(63)
$P_{ee,1-1}(1.5)$	35695.82464(33)	$Q_{fe,3-3}(3.5)$	35697.88923(65)	$Q_{fe,10-10}(10.5)$	35701.15511(98)
$P_{ff,4-5}(5.5)$	35696.48615(−27)	$R_{ee,5-4}(3.5)$	35697.89606(60)	$R_{ff,5-4}(4.5)$	35701.89159(−58)
$P_{ff,5-6}(5.5)$	35696.48856(−68)	$R_{ee,4-3}(3.5)$	35697.89898(15)	$R_{ff,6-5}(4.5)$	35701.89509(20)
$Q_{ef,5-5}(5.5)$	35696.49959(−54)	$Q_{fe,5-5}(4.5)$	35698.23331(4)	$Q_{fe,13-13}(12.5)$	35702.42881(−44)
$Q_{ef,3-3}(2.5)$	35696.51279(−88)	$Q_{fe,4-4}(4.5)$	35698.23966(50)	$Q_{fe,12-12}(12.5)$	35702.43403(−69)
$Q_{ef,6-6}(6.5)$	35696.57406(−28)	$R_{ee,6-5}(4.5)$	35698.24891(7)	$R_{ee,14-13}(12.5)$	35702.46610(21)
$Q_{ef,7-7}(6.5)$	35696.57870(−41)	$R_{ee,13-12}(4.5)$	35698.25347(59)	$R_{ee,13-12}(12.5)$	35702.46978(30)
$Q_{ef,7-7}(7.5)$	35696.68679(−42)	$Q_{fe,6-6}(5.5)$	35698.62135(−129)	$R_{ff,6-5}(5.5)$	35702.91321(−111)
$Q_{ef,8-8}(7.5)$	35696.69159(−44)	$Q_{fe,5-5}(5.5)$	35698.62810(−32)	$R_{ff,7-6}(5.5)$	35702.91830(117)

Table 2

The hyperfine-structure-resolved transitions in $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ of ^{206}PbF and ^{207}PbF by LIF spectroscopy. The residuals between observed and calculated transition frequencies are presented in the parentheses of observed frequency values (Obs.).

Label	Obs. (cm ⁻¹)	Label	Obs. (cm ⁻¹)	Label	Obs. (cm ⁻¹)
$P_{ee,12-13}(12.5)$	35690.05475(40)	$P_{ee,1-2}(2.5)$	35695.06728(−24)	$R_{ee,6-5}(4.5)$	35698.20946(−39)
$P_{ee,11-12}(12.5)$	35690.05808(−2)	$P_{ee,1-2}(1.5)$	35695.77668(6)	$R_{ee,5-4}(4.5)$	35698.21391(−12)
$P_{ee,11-12}(11.5)$	35690.38067(−24)	$R_{ee,4-3}(2.5)$	35697.54188(94)	$Q_{fe,7-7}(7.5)$	35699.48487(2)
$P_{ee,7-8}(8.5)$	35691.59670(−17)	$R_{ee,3-2}(2.5)$	35697.54607(41)	$R_{ee,9-8}(7.5)$	35699.50311(−6)
$P_{ee,7-8}(7.5)$	35692.07486(33)	$Q_{fe,4-4}(3.5)$	35697.84336(31)	$R_{ee,8-7}(7.5)$	35699.50739(31)
$P_{ee,3-4}(4.5)$	35693.75634(80)	$Q_{fe,3-3}(3.5)$	35697.84921(29)	$R_{ee,10-9}(8.5)$	35700.01136(−23)
$P_{ee,2-3}(3.5)$	35694.39192(−18)	$R_{ee,5-4}(3.5)$	35697.85609(2)	$R_{ee,9-8}(8.5)$	35700.01534(−12)
$P_{ee,2-3}(2.5)$	35695.06262(−19)	$R_{ee,4-3}(3.5)$	35697.85998(−46)	$R_{ff,5-4}(3.5)$	35700.87373(−53)
$Q_{fe,6-6,5-7,5}(7.5)$	35691.90055(55)	$P_{ee,1-2,0,5-1,5}(1.5)$	35695.61456(−96)	$R_{ee,4-3,3,5-2,5}(3.5)$	35697.68947(24)
$Q_{fe,4-6,4,5-5,5}(6.5)$	35692.42622(−43)	$P_{ee,1-1,0,5-0,5}(1.5)$	35695.62079(−91)	$R_{ee,5-4,4,5-4,5}(3.5)$	35697.80082(21)
$P_{ee,6-7,5-6,5}(6.5)$	35692.58201(−6)	$P_{ee,1-2,1,5-2,5}(1.5)$	35695.88765(−4)	$R_{ee,4-3,3,5-3,5}(3.5)$	35697.80569(5)
$P_{ee,5-6,4,5-5,5}(6.5)$	35692.58706(39)	$Q_{ef,4-4,3,5-4,5}(3.5)$	35696.25566(−17)	$Q_{fe,4-4,3,5-3,5}(3.5)$	35697.83708(−50)
$P_{ee,6-7,6,5-7,5}(6.5)$	35692.70740(−71)	$P_{ff,5-6,5,5-6,5}(5.5)$	35696.28575(−73)	$Q_{fe,5-5,5-4,5}(4.5)$	35698.03491(−48)
$P_{ee,5-6,5,5-6,5}(6.5)$	35692.71160(−37)	$Q_{ef,2-2,1,5-2,5}(2.5)$	35696.29525(35)	$Q_{fe,4-4,4,5-3,5}(4.5)$	35698.04024(−20)
$P_{ee,5-6,4,5-5,5}(5.5)$	35692.98171(−68)	$Q_{ff,3-3,2,5-3,5}(2.5)$	35696.29881(75)	$Q_{fe,6-6,6,5-5,5}(5.5)$	35698.42634(70)
$P_{ee,4-5,3,5-4,5}(5.5)$	35692.98646(−83)	$Q_{ef,5-5,4,5-4,5}(5.5)$	35696.56702(14)	$Q_{fe,5-5,5-4,5}(5.5)$	35698.43123(66)
$Q_{fe,4-6,4,5-5,5}(5.5)$	35693.14184(−59)	$Q_{ef,6-6,5,5-5,5}(5.5)$	35696.57053(−13)	$Q_{fe,6-6,6,5-6,5}(5.5)$	35698.54439(57)
$Q_{fe,3-5,3,5-4,5}(5.5)$	35693.14664(−45)	$P_{ff,8-9,7,5-8,5}(8.5)$	35696.89318(−31)	$Q_{fe,5-5,5-5,5}(5.5)$	35698.54948(81)
$P_{ee,4-5,3,5-4,5}(4.5)$	35693.58181(5)	$Q_{fe,0-1,0,5-1,5}(0.5)$	35697.13173(−47)	$S_{ef,4-2,3,5-2,5}(2.5)$	35699.75892(1)
$Q_{fe,3-5,3,5-4,5}(4.5)$	35693.74174(13)	$Q_{fe,1-1,1,5-1,5}(0.5)$	35697.13312(14)	$S_{ef,5-3,4,5-3,5}(2.5)$	35699.76229(25)
$Q_{fe,2-4,2,5-3,5}(4.5)$	35693.74611(−26)	$R_{ee,2-1,2,5-1,5}(0.5)$	35697.13539(−27)	$Q_{fe,10-10,10,5-9,5}(9.5)$	35700.37396(31)
$P_{ee,4-5,4,5-5,5}(4.5)$	35693.86483(62)	$Q_{fe,1-0,0,5-0,5}(0.5)$	35697.13725(44)	$Q_{fe,9-9,9,5-8,5}(9.5)$	35700.37817(−24)
$P_{ee,3-4,3,5-4,5}(4.5)$	35693.86860(39)	$Q_{fe,0-0,0,5-0,5}(0.5)$	35697.13936(74)	$R_{ff,6-5,6,5-5,5}(5.5)$	35702.71584(16)
$P_{ee,3-4,2,5-3,5}(3.5)$	35694.21943(−61)	$R_{ee,1-0,1,5-0,5}(0.5)$	35697.14135(10)	$R_{ff,7-6,7,5-6,5}(5.5)$	35702.71929(−2)
$P_{ee,2-3,1,5-2,5}(3.5)$	35694.22527(5)	$R_{ee,4-3,3,5-3,5}(2.5)$	35697.48637(−37)	$R_{ff,7-6,7,5-6,5}(6.5)$	35703.77820(−2)
$P_{ee,3-4,3,5-4,5}(3.5)$	35694.50069(50)	$R_{ee,3-2,2,5-2,5}(2.5)$	35697.49164(−30)	$R_{ff,8-7,8,5-7,5}(6.5)$	35703.78176(−14)
$P_{ee,2-3,2,5-3,5}(3.5)$	35694.50391(−40)	$Q_{fe,3-3,2,5-2,5}(2.5)$	35697.52677(18)	$R_{ff,8-7,8,5-7,5}(7.5)$	35704.87901(−28)
$P_{ee,2-3,1,5-2,5}(2.5)$	35694.89771(16)	$Q_{fe,3-3,3,5-3,5}(2.5)$	35697.64707(47)	$R_{ff,9-8,9,5-8,5}(7.5)$	35704.88316(14)
$P_{ee,1-2,0,5-1,5}(2.5)$	35694.90377(74)	$R_{ee,3-2,3,5-2,5}(2.5)$	35697.65558(−37)	$R_{ff,10-9,9,5-8,5}(9.5)$	35707.46601(−24)
$P_{ee,1-2,1,5-2,5}(2.5)$	35695.17978(73)	$R_{ee,5-4,4,5-3,5}(3.5)$	35697.68465(63)	$R_{ff,11-10,10,5-9,5}(9.5)$	35707.46954(17)

angular momentum quantum number. For transitions of the ^{207}PbF isotopologue, we need to consider the ^{207}Pb nuclear spin (1/2) in the designation to account for its hyperfine structures. These transitions are then denoted as $\Delta J_{q'q''} F_1'F_1, F_2'F_2(J)$, where F_2' or F_2 represents the good quantum number of the total angular momentum for the B or X_1 state including both nuclear spins of Pb and F.

4. Discussion

We treat the $X_1^2\Pi_{1/2}$ energy level structure in the Hund's case (a) basis set, and adopt its spin-rotational and hyperfine interaction Hamiltonians from Ref. [63]. For the $B^2\Sigma^+$ state of PbF, the Hund's case (b) coupling scheme is employed. The electron spin angular momentum S is

coupled to the spinless angular momentum $\mathbf{N}$ to form the total angular momentum $\mathbf{J} = \mathbf{N} + \mathbf{S}$. The spin-rotational Hamiltonian of the $B^2\Sigma^+$ state can then be expressed as [75]

$$\mathbf{H}_{\text{sr},B} = B\mathbf{N}^2 - D\mathbf{N}^4 + \gamma\mathbf{N} \cdot \mathbf{S}. \quad (1)$$

Here, B is the rotational constant, D is the centrifugal distortion constant, and γ is the spin-rotation constant. In the Hund's case (b) basis set, the excited-state energy levels can be expressed as

$$E_{\text{sr},B} = B\mathbf{N}(\mathbf{N}+1) - D[\mathbf{N}(\mathbf{N}+1)]^2 + \gamma(-1)^{N+J+S} \sqrt{S(S+1)(2S+1)} \sqrt{N(N+1)(2N+1)} \times \begin{Bmatrix} S & N & J \\ N & S & 1 \end{Bmatrix} + T_{00} \quad (2)$$

In addition, the hyperfine interaction Hamiltonian $\mathbf{H}_{\text{hfs},B}$ can be given as [76]

$$\mathbf{H}_{\text{hfs},B} = b_{F1}T^1(\hat{I}) \cdot T^1(\hat{S}) + c_1T^1_{q=0}(\hat{I})T^1_{q=0}(\hat{S}) + b_{F2}T^1(\hat{I}) \cdot T^1(\hat{S}) + c_2T^1_{q=0}(\hat{I})T^1_{q=0}(\hat{S}). \quad (3)$$

Here, the physically significant Fermi contact interaction constant $b_F = b + c/3$ with b and c representing the hyperfine constant and dipole-dipole interaction constant in Frosch and Foley parameters, while the nuclear spin-rotational constant C_N is generally negligible. The energy level structures of $X_1^2\Pi_{1/2}(v=0)$ and $B^2\Sigma^+(v'=0)$ can then be solved by analyzing the corresponding spin-rotational and hyperfine interaction Hamiltonians, based on preliminary ground- and excited-state molecular constants [63,64,77], followed by the tentative assignment of transitions in different rotational branches. To further optimize molecular constants for $B^2\Sigma^+(v'=0)$, an automatic fitting of molecular transitions was performed using the PGOPHER program [78]. We fit the experimental transitions of ^{206}PbF , ^{207}PbF , and ^{208}PbF by fixing the X_1 -state parameters to values reported in the ground-state microwave spectroscopy study by Mawhorter *et al.* [63], in order to obtain the B -state molecular constants as presented in Table 3. The fitted Frosch and Foley parameters $b(^{19}\text{F})$ and $c(^{19}\text{F})$ for the three PbF isotopologues are found to be 0.00189(26) cm^{-1} and 0.0031(13) cm^{-1} (^{208}PbF), 0.00163(53) cm^{-1} and 0.0022(13) cm^{-1} (^{207}PbF), and 0.00155(31) cm^{-1} and 0.0033(17) cm^{-1} (^{206}PbF), respectively. For the $B^2\Sigma^+$ state of ^{207}PbF , $b(^{207}\text{Pb})$ and $c(^{207}\text{Pb})$ are determined to be 0.15980(11) cm^{-1} and 0.00204(31) cm^{-1} . Although the hyperfine interaction between the nuclear and electronic magnetic moments is often described in the Frosch and Foley parameters, it shall provide analytical convenience to express the hyperfine interaction terms in the molecular body-fixed frame. For the $B^2\Sigma^+$ state, hyperfine constants $A_{\parallel}$ and $A_{\perp}$ are connected to Frosch and Foley parameters as $A_{\parallel} = b + c$ and $A_{\perp} = b$, which have been converted in Table 3. Here, the hyperfine interaction parameters due to the ^{19}F nucleus ($A_{\perp}$ and $A_{\parallel}$) of $B^2\Sigma^+(v'=0)$ state are reported for the first time and those due to the ^{207}Pb nucleus ($A_{\perp}$ and $A_{\parallel}$) have been also updated, showing improved accuracy compared with reported values in the supersonic molecular beam experiment of PbF [64] due to better spectral linewidth of the BGC experiment.

5. Conclusions

To summarize, we demonstrated the production of a cryogenic PbF molecular beam in the BGC apparatus, and carried out high-resolution laser spectroscopy measurements in its $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ transition, including both direct absorption and LIF spectroscopy. The Doppler-broadened absorption spectrum exhibits the transition profile of about 221 MHz linewidth, however, LIF spectrum of the cryogenic PbF molecular beam demonstrates its central forward velocity of 223 ± 17 m/s and reveal broader spectral range as well as better resolved transition lines. In the LIF spectrum of $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$,

Table 3

The rotational and hyperfine constants (cm^{-1}) for the $B^2\Sigma^+(v'=0)$ state of PbF.

Parameter	^{206}PbF	^{207}PbF	^{208}PbF
B	0.2475529(22)	0.2474436(15)	0.2473434(43)
	0.2475375(16) ^a	0.2474495(76) ^a	0.2473225(57) ^a
$10^7 \times D$	1.84(11)	1.88(23)	1.83(25)
	1.475(23) ^a	1.619(4) ^a	1.617(15) ^a
γ	0.002698(33)	0.002609(68)	0.002641(21)
	0.002716(22) ^a	0.002732(13) ^a	0.002653(16) ^a
$A_{\perp}(^{19}\text{F})$	0.00155(31)	0.00163(53)	0.00189(26)
$A_{\parallel}(^{19}\text{F})$	0.0048(20)	0.0038(18)	0.0050(16)
$A_{\perp}(^{207}\text{Pb})$		0.15980(11)	
		0.1584(17) ^a	
$A_{\parallel}(^{207}\text{Pb})$		0.16184(42)	
		0.1644(21) ^a	
T_{00}	31558.90815(11)	31558.923640(71)	31558.95620(13)

^a Converted from Reference [64].

81, 66 and 24 hyperfine-structure-resolved spectral lines with the line-width of 120 MHz and a frequency accuracy of 40 MHz have been assigned, respectively, for ^{208}PbF , ^{207}PbF and ^{206}PbF molecules. The hyperfine constants due to the ^{19}F nucleus of the $B^2\Sigma^+(v'=0)$ state are reported for the first time, and those due to the ^{207}Pb nucleus have been also updated, exhibiting better accuracy owing to the narrower line-width of the BGC technique. Such a cryogenic molecular beam of PbF in association with its hyperfine-structure-resolved spectral atlas in $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ will be essential in developing the sensitive detection schemes of the eEDM measurement. The slow forward velocity facilitates longer coherence time and improved sensitivity for the eEDM phase detection, and enables the feasibility of Stark deceleration and laser-cooling. In addition, the buffer-gas-cooled molecular beam exhibits lower rotational temperature such that the preparation of the eEDM superposition state that requires higher population in the $J=1/2$ ground state can be more readily available. Our narrower spectral linewidth can not only reveal hyperfine-structure-resolved molecular transitions with better frequency measurement, but also enlighten the detection of the $A^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ transition within which the excited A-state has a much longer radiative lifetime of 5 μs compared to the $B^2\Sigma^+$ state value of 2 ns [60,66]. Our demonstrated buffer-gas-cooled PbF molecular beam source as well as its spectroscopic characterization in the $B^2\Sigma^+(v'=0) \leftarrow X_1^2\Pi_{1/2}(v=0)$ transition will eventually contribute to the spectroscopic detection schemes of precision measurement of eEDM using PbF molecules.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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