Optical clock spectroscopy in weakly bound molecules

Mateusz Borkowski
Institute of Physics, Faculty of Physics, Astronomy and Informatics,
Nicolaus Copernicus University, Grudziadzka 5, 87-100 Toruń, Poland
E-mail: mateusz@fizyka.umk.pl

Abstract. With relative accuracies reaching $10^{-18}$, optical atomic clocks are currently the most sensitive physical instruments known to man. Weakly bound ultracold molecules enable the study of fundamental physics through their sensitivity to e.g. the proton-to-electron mass ratio or hypothetical Yukawa-type fifth forces predicted by several extensions of the Standard Model. These applications, however, require precision measurements of molecular transitions that are beyond current experimental capabilities. Here we propose to construct an ‘optical molecular clock’ that would solve this problem by bringing the experimental techniques used in optical atomic clocks to the realm of cold molecules. We show that such a clock could utilize ultracold ytterbium molecules and we predict the positions and properties of Yb$_2$ clock lines. A successful experimental realization of this proposal could pave the way towards sub-Hz level molecular spectroscopy.

1. Introduction
Optical lattice clocks [1–5], capable of measuring time and frequency at a relative accuracy now exceeding $10^{-18}$, are the most accurate physical instruments to date. Apart from their obvious application as frequency standards they have found use in testing the fundamentals of physics [6], placing limits on the temporal variations of fundamental constants [7], exploring quantum many-body systems [8–11], or even searching for dark matter [12].

Weakly bound molecules composed of the two-valence-electron atoms used in optical atomic clocks have been the subject of substantial experimental attention thanks to the narrow intercombination line that facilitates high resolution spectroscopy. The positions of vibrational states in such molecules were investigated by means of one- and two-color photoassociation spectroscopy [13] in both strontium [14–16] and ytterbium [17–19]. Ultracold samples of stable ground state molecules $^{88}$Sr$_2$ [20], $^{84}$Sr$_2$ [16] and $^{174}$Yb$_2$ [21] have also been produced. Weakly bound molecules have been used as prototype systems for studies of fundamental physics. For instance, subradiance has been investigated using the Laporte-rule-forbidden $g \rightarrow g$ transitions in both Yb$_2$ [22] and Sr$_2$ [23] molecules. Recent Yb$_2$ photoassociation data has been used to investigate beyond-Born-Oppenheimer physics [19]. Diatomic molecules have been proposed to be used to search for variations in the proton-to-electron mass ratio [24] and fifth forces [25, 26]. These applications of weakly bound molecules, however, rely on high precision measurements of either a molecular line or, directly, bound state positions. Currently the most accurate measurements of vibrational state positions in these molecules achieve error bars on the order of hundreds of Hz [16, 19, 27]. Here, we propose to use a molecular analogue of optical atomic clock spectroscopy using ultracold Yb$_2$ molecules to achieve accuracies possibly orders of magnitude better than previously.
Figure 1. a. Operation of an optical lattice clock utilizing bosonic atoms. A weak external magnetic field is used to induce nondiagonal Zeeman mixing $\Omega_B$ of dark $^3P_0$ and bright $^3P_1$ atomic states. As a result, the mixed clock state $^3P_0\tilde{\rho}$ "borrows" a bit of the transition dipole moment from the bright $^3P_1$ state and Rabi oscillations between the ground and clock states can be induced. The oscillation frequency $\Omega_{at}$ is given by Eq. (1). b. An extension to the molecular case. Asymptotically the molecular ground and excited states may be expressed as product states of relevant atomic states, together with appropriate wavefunctions $\Psi_{g,e}(R)$ and spherical harmonics $Y_{m,l}(\theta, \phi)$ to describe the radial and rotational motion of the diatomic molecule. The symmetrized ungerade excited wavefunction is comprised of the ground $^1S_0$ and the Zeeman-mixed $^3P_0\tilde{\rho}$ states to account for the effect of the external magnetic field. The frequency of the Rabi oscillations, $\Omega_{mol}$, is given by Eq. (2).

2. Magnetically induced clock spectroscopy

At the heart of a lattice clock lies the spectroscopy (Fig. 1) of ultranarrow $^1S_0 \leftrightarrow ^3P_0$ transition in atoms confined to an optical lattice. The transition itself is forbidden due to the change of total spin and the $J = 0 \not\leftrightarrow 0$ selection rules. In fermionic species, this transition is weakly allowed as hyperfine interactions dress the $^3P_0$ state with an admixture of nearby optically active $^3P_1$ and $^1P_1$ states [28]. In bosons, however, this transition is prohibitively weak. To mitigate this, one can use an external magnetic field [29, 30] to induce a similar dressing of the $^3P_0$ atomic state: $\ket{^3P_0} \approx \ket{^3P_0} + \frac{\Omega_B}{\Delta} \ket{^3P_1}$. The nondiagonal Zeeman matrix element $\Omega_B$ is proportional to the applied magnetic field $B$, whereas $\Delta$ is the fine splitting between the $^3P_0$ and $^3P_1$ states. In experiments the magnetic fields routinely used are on the order of 1 mT to avoid uncertainties due to the quadratic Zeeman effect; in these conditions the natural linewidth of the clock transition is on the order of a $\mu$Hz. The effective transition dipole moment, however, is large enough for a laser to induce Rabi oscillations between the ground $^1S_0$ and the dressed $^3P_0$ states. The oscillation frequency, assuming parallel magnetic fields and light polarizations, is

$$\Omega_{at} = \alpha \sqrt{T|\vec{B}|}.$$  (1)
The quantity $\alpha$ depends on the atom used and for Yb is equal to [29] $\alpha_{\text{Yb}} = 186 \text{ Hz/T}\sqrt{\text{mW/cm}^2}$. In practical experimental realizations $\Omega_{\text{at}}$ is on the order of Hz to allow for an interrogation time comparable to the lifetime of atoms in the lattice, typically several seconds.

We propose [31] that the same mechanism could be applied to weakly bound diatomic molecules composed of atoms used in bosonic atomic clocks (Figure 1b). The ground molecular state would be composed, asymptotically, of two atoms in the $^1S_0$ electronic state. The appropriate molecular state in the atomic basis can be written as a simple product, $|g\rangle = |^1S_0\rangle_A |^1S_0\rangle_B \Psi_g(R) Y_{l}^m(\theta, \phi)$, which in Hund’s case (c) representation appropriate for weakly bound molecules corresponds to the X $^0_g^+$ state [13, 32]. The radial wavefunction $\Psi_g(R)$ represents the vibrational motion in the molecule, while the spherical harmonic $Y_{l}^m(\theta, \phi)$ corresponds to end-over-end rotational motion of the molecule. From now on we will only consider rotationless states with $l = m_l = 0$. If we were to excite the atomic pair with a single photon, again utilizing a magnetic field to dress the $^3P_0$ state, the appropriate asymptotic wavefunction could be $|\hat{e}\rangle = \frac{1}{\sqrt{2}} \left( |^3P_0\rangle_A |^1S_0\rangle_B + |^1S_0\rangle_A |^3P_0\rangle_B \right) \Psi_e(R) Y_{l}^m(\theta, \phi)$. Since the two atoms are identical bosons, the excitation has to be shared equally to obtain the correct wavefunction symmetry. This state corresponds to a Hund’s case (c) $0_u^-$ molecular state with total angular momentum $\mathbf{J} = \mathbf{j} + \mathbf{l}$ equal to zero. In principle, the same expression, but with a ‘−’ sign could also denote a correct molecular state – the $0_u^-$ state – but due to symmetry considerations [32, 33], this state does not exist for $J = 0$ in a homonuclear molecule. Also, such states would be even more challenging to observe from the $0_g^+$ ground state as the Laporte rule forbids electric-dipole transitions between states of the same parity [22, 23, 32].

For weakly bound molecules one can easily derive an approximate expression for the frequency of laser induced molecular Rabi oscillations [31]. In these molecules atoms spend most of the time at large separations $R$, on the order of 50–100 $a_0$, where atomic interactions are very weak compared to the splittings between atomic energy levels. It is therefore reasonable to approximate the ($R$-dependent) splitting between $^3P_0$ and $^3P_1$ states with the atomic value. We can also assume that the Zeeman matrix element $\Omega_B$ is also distance independent. This way the admixture of the $^3P_1$ state in the dressed $^3P_0$ state becomes approximately independent of $R$. Finally, at distances large enough for the electronic clouds not to overlap, but smaller than the transition wavelength to avoid retardation effects, the molecular transition dipole moment operator can be approximated with its atomic counterparts: $d_{\text{mol}} = d_{\text{at}}^A + d_{\text{at}}^B$ [34]. Thus, through direct calculation, it can be shown that

$$\Omega_{\text{mol}} = \sqrt{2}\sqrt{\Omega_{\text{FC}}\Omega_{\text{at}}}.$$  

The $\sqrt{2}$ results from this being, ironically, a superradiant ultranarrow transition between states of $g$ and $u$ symmetry. The quantity $f_{\text{FC}}$ is a standard Franck-Condon factor, i.e. an overlap integral between ground and excited vibrational wavefunctions, $f_{\text{FC}} = \int_0^{\infty} \Psi_g(R)\Psi_e(R)dR$. Finally, $\Omega_{\text{at}}$ is the atomic Rabi frequency under the same magnetic field and laser intensity. This is a parameter experimentalists already have control over and the crucial quantity that determines whether or not the observation of a clock transition would be experimentally viable, is the Franck-Condon factor $f_{\text{FC}}$. For example, to observe a hypothetical transition characterised by $f_{\text{FC}}$ on the order of $10^{-2}$, would require a magnetic field that is an order of magnitude larger than that for atoms to get the same Rabi frequency (because $\Omega_{\text{mol}} \propto \sqrt{f_{\text{FC}}}$ and $\Omega_{\text{mol}} \propto B$). Alternatively, the low Franck-Condon factor could be compensated for by increasing the laser intensity by two orders of magnitude (because $\Omega_{\text{mol}} \propto \sqrt{I}$).

3. Predictions for the Yb$_2$ molecule

For bosonic systems, the positions of bound states near the $^1S_0 \rightarrow ^3P_0$ asymptote have not been observed so far. For the $^{174}$Yb$_2$ molecule, however, the positions of near-threshold vibrational
states can be predicted theoretically [31], using the close relationship between s-wave scattering lengths and near-threshold bound states [13, 36, 37]. This relationship is routinely used to determine s-wave scattering lengths from two-color photoassociation spectroscopy experiments. Typically a model potential \( V(R) \) is constructed so that the theoretical bound state energies calculated by solving an appropriate radial Schrödinger equation, e.g.,

\[
\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) \right) \Psi(R) = E \Psi(R),
\]

match experimental data. Then, the same potential is used to calculate the s-wave scattering lengths. Here, we employ the same relationship, just in the opposite direction. We use the recent measurements of the s-wave scattering lengths in the ground-ground and ground-excited state collisions of Yb atoms and \textit{ab initio} long range potential coefficients [35] to determine the positions of near-threshold bound states near the molecular \(^1\text{S}_0 + ^3\text{P}_0\) clock asymptote.

According to the LeRoy-Bernstein theory [38], the near-threshold vibrational spectrum is chiefly described by the long range van der Waals coefficient \( C_6 \), which determines the vibrational spacing, and the total phase of the radial wavefunction, which sets a “starting point” for the spectrum. Porsev \textit{et al.} [35] give the value of the long range van der Waals coefficients \( C_6 = 2561(95) E_h a_0^6 \), the second order van der Waals interaction term, \( C_8 = 3.81(0.21) \times 10^5 E_h a_0^8 \), provides a valuable correction to the vibrational spacings and can be calculated from the \( C_8 \) values of \( 3.20(0.14) \times 10^5 E_h a_0^8 \) and \( 4.11(0.18) \times 10^5 E_h a_0^8 \) given in [35] for the respective \(^1\text{S}_0 + ^3\text{P}_1\) \(^0_u\) and \(^1_u\) potentials using the asymptotic relations [32] of these curves with the nonrelativistic \(^3\Sigma_u^+\) and \(^3\Pi_u\) potentials. The total phase of the radial wavefunction can be fixed by adjusting the short range parameter \( \sigma \) of the model potential, \( V(R) = -C_8(0^-)R^{-8} - (1 - (\sigma/R)^6)C_6(0^-)R^{-6} \), in such a way that its s-wave scattering length matches the experimental value of \( a_{ge} = +94.84(0.14) a_0 \) based on a recent measurement of \((a_{ge} - a_{gg}) = -10.19(0.13) a_0 \) [9] and \( a_{gg} = +105.0332(95) a_0 \) [19]. Using these parameters one can determine the positions of excited clock bound states shown in Figure 2. The estimated accuracy of this prediction reaches tens of
Atoms: 5.9 kHz for the least bound state, several MHz for the second and about 20 MHz for the third. The predicted values should be useful as starting points for the experimental search.

The chances of observing the predicted clock states depend on the Franck-Condon factor $f_{FC}$. For direct photoassociation of two unbound ground state atoms in an optical lattice site, $f_{FC}$ is on the order of $10^{-6} - 10^{-5}$. Thus, it would require a significantly more intense laser and/or magnetic field to perform the clock spectroscopy this way, and would be a challenge to perform with existing atomic clock setups. Much better Franck-Condon factors characterize bound-bound transitions between weakly bound states in ground and excited electronic states of a molecule. The positions of ground-state near-threshold states in Yb$_2$, also shown in Figure 2, have been recently measured to high accuracy by two-color photoassociation spectroscopy [19]. For three vibrational states in both ground and excited electronic states there are, of course, nine possible molecular lines. Their positions, with respect to the 578 nm atomic clock line, and respective Franck-Condon factors are given in Table 1. Six of these have $f_{FC}$ over 0.01. Under a very reasonable magnetic field $|B| = 1$ mT and laser intensity $I = 1$ W/cm$^2$ one could observe molecular Rabi frequencies of a few Hz which is comparable to the value of 5.9 Hz expected for the clock transitions in Yb atoms under same experimental conditions. Also, all reported lines are within less than 2 GHz from the atomic clock line, so in principle it should be possible to even use the same clock laser to observe both the atomic and molecular clock transitions in an existing experimental setup.

4. Conclusion and outlook

This proposal, if realized, would bring the technology utilized in optical atomic clocks to weakly bound molecules. Currently, the most accurate optical measurements of bound state or molecular line positions are on the order of a few hundred Hz [16, 19, 27]. On the other hand, current optical atomic clocks routinely achieve an accuracy of better than 1 Hz in a matter of seconds (see e.g. refs. [4, 5]). An optical molecular clock could therefore be utilized to measure vibrational spacings in a ground state molecule to an accuracy at least two orders of magnitude better than previously. Possible uses for such accurate molecular measurements include searching for fifth forces [26] or temporal variations in the proton-to-electron mass ratio [24, 39], testing the Born-Oppenheimer approximation [19, 40, 41] or relativistic corrections to long range atomic interactions [42–44].

The bosonic ytterbium molecule is a prime candidate for the practical realization of this proposal. Laser cooling techniques for ytterbium are well established, resulting in the production of degenerate gases in most of its isotopes [45–48]. The isotope $^{174}$Yb was the original bosonic species where magnetically induced clock spectroscopy was realized experimentally [30]. Clock spectroscopy of Yb gases in 3D optical lattices was recently performed in two separate laboratories [9, 10]. Stable weakly bound ground state molecules necessary for this proposal have

| $v'_g$ | $v'_e$ | $\Delta$ (MHz) | $f_{FC}$ | $\Omega_{mol}^{th}$ (Hz) |
|-------|-------|----------------|---------|---------------------|
| -1    | -1    | -3.130(43)     | 0.9495  | 8.1                 |
| -1    | -2    | -311.8(4.2)    | 0.0217  | 1.2                 |
| -1    | -3    | -1428(23)      | 0.0166  | 1.1                 |
| -2    | -1    | +311.908(43)   | 0.0009  | 0.2                 |
| -2    | -2    | +3.2(4.2)      | 0.6755  | 6.8                 |
| -2    | -3    | -1113(23)      | 0.2140  | 3.8                 |
| -3    | -1    | +1514.130(43)  | 0.0002  | 0.1                 |
| -3    | -2    | +1205.4(4.2)   | 0.0025  | 0.4                 |
| -3    | -3    | +89(23)        | 0.3990  | 5.2                 |

Table 1. Positions $\Delta$ of molecular clock lines in $^{174}$Yb$_2$ with respect to the 578 nm $^1S_0 \leftrightarrow ^3P_0$ clock transitions. Theoretical molecular Rabi oscillation frequencies are given for $|B| = 1$ mT (10 G) and $I = 1$ W/cm$^2$. Vibrational quantum numbers in electronic ground and excited states $v'_g$ and $v'_e$ are counted down from the respective dissociation limits.
been produced by spontaneous emission following intercombination line photoassociation [21], but we have also shown that StiRAP [49] can produce these molecules efficiently from unbound atomic pairs in 3D optical lattice sites. Finally, the accurate theoretical prediction [31] of molecular clock line positions and their properties will provide excellent guidance for future experiments.

Acknowledgments
This research was supported by the National Science Centre, Grant nos. 2014/13/N/ST2/02591 and 2017/25/B/ST4/01486. Support has been received from the project EMPIR 15SIB03 OC18. This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme. It is part of an ongoing research program of the National Laboratory FAMO in Toruń, Poland. Calculations have been carried out in the Wroclaw Centre for Networking and Supercomputing, Grant no. 353.

References
[1] Takamoto M, Hong F L, Higashi R and Katori H 2005 Nature 435 321–324
[2] Katori H 2011 Nature Photonics 5 203–210
[3] Ludlow A D, Boyd M M, Ye J, Peik E and Schmidt P O 2015 Reviews of Modern Physics 87 638
[4] Nicholson T, Campbell S, Hutson R, Marti G, Bloom B, McNally R, Zhang W, Barrett M, Safronova M, Strouse G, Tew W and Ye J 2015 Nature Communications 6 6896
[5] McGrew W F, Zhang X, Fiasano R J, Schäffer S A, Beloy K, Nicolodi D, Brown R C, Hinkley N, Milani G, Schioppo M, Yoon T H and Ludlow A D 2018 Nature 564 87–90
[6] Chou C W, Hume D B, Rosenband T and Wineland D J 2010 Science 329 1630–1633
[7] Blatt S, Ludlow A D, Campbell G K, Thomsen J W, Zelevinsky T, Boyd M M, Ye J, Baillard X, Fouché M, Le Targat R, Brusch A, Lemonde P, Takamoto M, Hong F L, Katori H and Flambaum V V 2008 Physical Review Letters 100 140801
[8] Rey A, Gorshkov A, Kraus C, Martin M, Bishop M, Zhang X, Benko C, Ye J, Lemke N and Ludlow A 2014 Annals of Physics 340 311–351
[9] Franchi L, Livi L F, Cappellini G, Binella G, Inguscio M, Catani J and Fallani L 2017 New J. Phys. 19 103037
[10] Bouganne R, Aguileta M B, Dareau A, Soave E, Beugnon J and Gerbier F 2017 New J. Phys. 19 113006
[11] Goban A, Hutson R B, Marti G E, Campbell S L, Perlin M A, Julienne P S, D’Incao J P, Rey A M and Ye J 2018 Nature 563 369–373
[12] Weislo P, Morzyński P, Bober M, Cygan A, Lisak D, Ciuryło R and Zawada M 2016 Nature Astronomy 1 0009
[13] Jones K M, Tiesinga E, Lett P D and Julienne P S 2006 Reviews of Modern Physics 78 483–535
[14] Zelevinsky T, Boyd M M, Ludlow A D, Ido T, Ye J, Ciuryłø R, Naidon P and Julienne P S 2006 Physical Review Letters 96 203201 (Preprint 0602135)
[15] Borkowski M, Morzyński P, Ciuryłø R, Julienne P S, Yan M, Desalvo B J and Killian T C 2014 Phys. Rev. A 90 032713
[16] Stellmer S, Pasquio B, Grimm R and Schreck F 2012 Physical Review Letters 109 115302
[17] Tojo S, Kitagawa M, Enomoto K, Kato Y, Takasu Y, Kumakura M and Takahashi Y 2006 Physical Review Letters 96 153201
[18] Borkowski M, Ciuryłø R, Julienne P S, Tojo S, Enomoto K and Takahashi Y 2009 Physical Review A 80 012715
[19] Borkowski M, Buchachenko A A, Ciuryło R, Julienne P S, Yamada H, Kikuchi Y, Takahashi K, Takasu Y and Takahashi Y 2017 Phys. Rev. A 96 063405
[20] Reinaudi G, Osborn C B, McDonald M, Kotochigova S and Zelevinsky T 2012 Physical Review Letters 109 115303
[21] Kato S, Yamazaki R, Shibata K, Yamamoto R, Yamada H and Takahashi Y 2012 Physical Review A 86 043411
[22] Takasu Y, Saito Y, Takahashi Y, Borkowski M, Ciurylo R and Julienne P S 2012 Phys. Rev. Lett. 108 173002
[23] McGuyer B H, McDonald M, Iwata G Z, Tarallo M G, Skomorowski W, Moszynski R and Zelevinsky T 2008 Phys. Rev. Lett. 100 043201
[24] Salumbides E J, Koelemeij J C J, Komasa J, Pachucki K, Eikema K S E and Ubachs W 2013 Phys. Rev. D 87 112008
[25] Borkowski M, Buchachenko A A, Ciuryło R, Julienne P S, Yamada H, Y uu K, Takahashi K, Takasu Y and Takahashi Y 2017 Journal of Physics: Conference Series 810 012014
[26] McGuyer B H, McDonald M, Iwata G Z, Tarallo M G, Grier A T, Apfelbeck F and Zelevinsky T 2015 New J. Phys 17 055004
[27] Borkowski M, Buchachenko A A, Ciuryło R, Julienne P S, Yamada H, Kikuchi Y, Takahashi K, Takasu Y and Takahashi Y 2017 Physica Scripta: Conference Series 810 012014
[28] McGuyer B H, McDonald M, Iwata G Z, Tarallo M G, Grier A T, Apfelbeck F and Zelevinsky T 2015 Phys. Rev. Lett. 108 173002
[29] Barber Z W, Hoyt C W, Oates C W, Hollberg L 2006 Physical Review Letters 96 083002
[30] Barber Z W, Hoyt C W, Oates C W, Hollberg L, Taichenachev A V and Yudin V I 2006 Phys. Rev. Lett. 96 083002
[31] Borkowski M 2018 Physical Review Letters 120 083202
[32] Mies F H, Stevens W J and Krauss M 1978 Journal of Molecular Spectroscopy 72 303–331
[33] Bussery-Houvault B, Launay J M, Korona T and Moszynski R 2006 The Journal of Chemical Physics 125 114315
[34] Power E A 1967 The Journal of Chemical Physics 46 4297–4298
[35] Porsev S G, Safronova M S, Derevianko A and Clark C W 2014 Physical Review A 89 012711
[36] Kitagawa M, Enomoto K, Kasa K, Takahashi Y, Ciurylo R, Naidon P and Julienne P S 2008 Physical Review A 77 021719
[37] Borkowski M, Żuchowski P S, Ciuryło R, Julienne P S, Kędziera D, Mentel L, Tecmer P, Münchow F, Bruni C and Götitz A 2013 Phys. Rev. A 88 052708
[38] Le Roy R J and Bernstein R B 1970 The Journal of Chemical Physics 52 3869
[39] Demille D, Sainis S, Sage J, Bergeman T, Kotochigova S and Tiesinga E 2008 Physical Review Letters 100 043202
[40] Born M and Huang K 1956 Dynamical Theory of Crystal Lattices (New York: Oxford University)
[41] Lutz J J and Hutson J M 2016 Journal of Molecular Spectroscopy 330 43–56
[42] Casimir H B G and Polder D 1948 Physical Review 73 360–372
[43] Zhang P and Dalgarno A 2008 Molecular Physics 106 1525–1529
[44] Balcerzak J G, Lesiuk M and Moszynski R 2017 Physical Review A 96 052510
[45] Takasu Y, Maki K, Komori K, Takano T, Honda K, Kumakura M, Yabuzaki T and Takahashi Y 2003 Physical Review Letters 91 040404
[46] Sugawa S, Yamazaki R, Taie S and Takahashi Y 2011 Physical Review A 84 011610(R)
[47] Fukuhara T, Sugawa S and Takahashi Y 2007 Physical Review A 76 051604(R)
[48] Fukuhara T, Sugawa S, Takasu Y and Takahashi Y 2009 Physical Review A 79 021601(R)
[49] Bergmann K, Theuer H and Shore B W 1998 Reviews of Modern Physics 70 1003–1025