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Towards detection of the molecular parity violation in chiral Ru(acac)₃ and Os(acac)₃

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Investigations into the helically chiral compound Ru(acac)₃ shows potential for the experimental detection of parity violation (PV) in a molecular system. An experimental set-up for measuring PV frequency shifts $\Delta\nu^{\text{PV}}$ in vibrational spectra of Ru(acac)₃ is currently being built at Laboratoire de Physique des Lasers in Paris. Based on our relativistic calculations, the most promising vibrational modes are identified with fractional shifts $\Delta\nu^{\text{PV}}/\nu$ reaching up to two orders of magnitude higher ($\sim 10^{-13}$) compared to the projected instrumental sensitivity ($\sim 10^{-15}$). The related heavier homologue Os(acac)₃ exhibits even higher relative PV shifts extending up to $\Delta\nu^{\text{PV}}/\nu \sim 10^{-12}$ strongly motivating its future synthesis and characterization.

Introduction. – Parity violation (PV) through electro-weak interactions was first predicted in 1956 [1], immediately afterwards observed in nuclear physics [2, 3], and later in atomic physics [4–7]. In chiral molecules, the exchange of the heavy neutral Z^0 gauge boson between the electrons and the nuclei is predicted to result in a tiny energy difference between the two enantiomers. Due to this energy difference, the lower-energy enantiomer would be present in slight excess in an equilibrium mixture; this imbalance may provide a clue to the origin of biomolecular homochirality, *i.e.* why chiral molecules usually occur in only one enantiomeric form in nature [8–10].

Over the past decades, various experiments have been proposed to observe parity violation in chiral molecules, including measurements of PV frequency shifts in NMR spectroscopy (*e.g.* [11–14]), measurements of the time-dependence of optical activity [15], and direct measurement of the absolute PV energy shift of the electronic ground state [16]; see also the reviews by Berger and Stohner [17], Berger [18], and Schwerdtfeger [19]. However, for none of the aforementioned experimental

schemes, tight experimental upper bounds have been reported yet [17]; this has only been accomplished in measurements of the PV shift of vibrational frequencies, performed at the Laboratoire de Physique des Lasers (LPL) in Paris [20–24], using ultra-precise mid-infrared molecular spectroscopy experiments.

Several molecules have been considered as candidates for experiments at LPL. The first experiments were performed on the C–F stretch vibration in CHFClBr lying conveniently in the CO₂ laser frequency range [20, 21, 25, 26], but led to a non-detection, with an upper limit of $\Delta\nu^{\text{PV}}/\nu = 2.5 \times 10^{-13}$, with ν the vibrational transition frequency and $\Delta\nu^{\text{PV}}$ the parity violating frequency difference between enantiomers. Later, *ab initio* calculations predicted the PV shift for this transition to be 3 to 4 orders of magnitude smaller [27–30]. Another fluorohalomethane that has been under investigation, CHFClI, is predicted to have a larger PV shift, but is not stable enough for measurements [22, 31].

Other candidate molecules include SeOClI [32], N≡WHClI [33], and N≡UHXY [34] (X, Y = F, Cl, Br, I). These systems were predicted to possess vibrational transitions with progressively larger PV shifts, as large as several tens of Hz (or $\Delta\nu^{\text{PV}}/\nu \sim 10^{-13}$) in N≡UHFI. So far, the synthesis of these compounds has not

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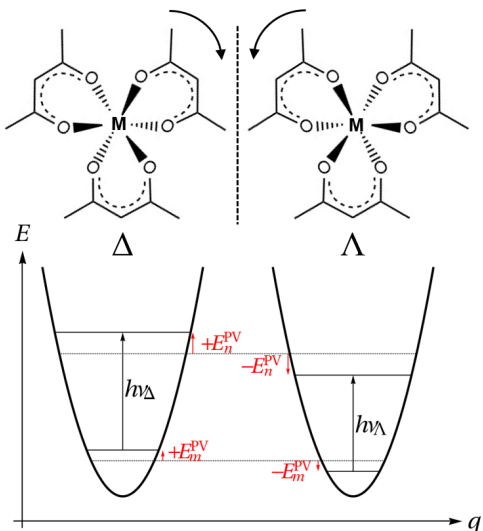


FIG. 1. Chemical structures of the Δ - and Λ - $M(\text{acac})_3$ ($M = \text{Ru}, \text{Os}$) with the corresponding transition frequencies ν_Δ and ν_Λ .

been reported. More recently, attention has turned to chiral oxorhenium complexes [35, 36], but bringing these into the gas phase required for high-precision spectroscopy remains a challenge given their low stability.

Currently under investigation and subject of this paper are the propeller-like chiral complexes ruthenium(III) acetylacetonate $\text{Ru}(\text{acac})_3$ and its heavier homologue osmium(III) acetylacetonate $\text{Os}(\text{acac})_3$ (Fig. 1). Ruthenium ($Z = 44$) is a reasonably heavy nucleus, so that in accord with the proposed Z^5 -scaling law [34, 37, 38] we expect this system to experience a large absolute PV energy shift. Furthermore, this complex is commercially available in its racemic form, it can be readily resolved into pure Δ and Λ enantiomers at gram scales [39], and has been characterized through its chiroptical activity [40]. Another appealing aspect of $\text{Ru}(\text{acac})_3$ is its relatively high volatility, which has proven very useful for preparation of metallic surfaces for catalytic and optoelectronic applications through sublimation and chemical vapour deposition [41, 42]. It is stable and robust under evaporation by heating up to 200°C , and can thus be brought into the gas phase. We have recently been able to seed it in a molecular beam, allowing us to carry out photoelectron spectroscopy and photoelectron circular dichroism measurements [43]. All in all, these factors make it an attractive candidate for gas-phase spectroscopy experiments. It should in particular survive laser ablation and allow the production of intense sources of cold and slow gas samples via buffer-gas cooling in a cryogenic chamber, a method that we have recently demonstrated with organo-metallic species [24, 44, 45]. The characterization of $\text{Ru}(\text{acac})_3$ in the mid-infrared region is ongoing and we report preliminary Fourier transform spectroscopic investigations in solid neon at 3 K,

that in combination with the present calculations allow us to select the most appropriate transitions for measuring parity violation.

The heavier homologue of $\text{Ru}(\text{acac})_3$, $\text{Os}(\text{acac})_3$, is not commercially available but can be synthesised [46]. Its higher atomic number will most likely lead to larger vibrational PV shifts [34], making it a promising alternative to $\text{Ru}(\text{acac})_3$.

In this work, we perform theoretical investigations of the magnitude of the PV shifts that can be expected in $\text{Ru}(\text{acac})_3$ and $\text{Os}(\text{acac})_3$ and guide the selection of suitable vibrational modes for measurements; this will determine the frequency range for the laser system to be built and tuned at LPL. Such *a priori* investigations are crucial, as the size of the PV vibrational shift can vary by over an order of magnitude, depending on the vibrational mode [30].

Theory. – According to the standard model of particle physics, the dominant P -odd contribution of the weak force to the molecular Hamiltonian is due to vector-nucleonic-axial-vector-electronic coupling. In the low-energy limit, the following nuclear spin-independent effective Hamiltonian can be derived from the standard model Lagrangian (see *e.g.* Refs. [18, 47]):

$$\hat{H}^{\text{PV}} = \frac{G_{\text{F}}}{2\sqrt{2}} \sum_j^{\text{electrons}} \sum_A^{\text{nuclei}} Q_{\text{W}}(A) \gamma_j^5 \rho(\mathbf{r}_j - \mathbf{r}_A), \quad (1)$$

which is compatible with the usual four-component framework for relativistic quantum chemical calculations. In this equation, $G_{\text{F}} = 2.22255 \times 10^{-14} E_{\text{h}} a_0^3$ with E_{h} the Hartree energy and a_0 the Bohr radius, stands for the Fermi coupling constant; the weak charge of nucleus A is given by $Q_{\text{W}}(A) = [(1 - 4 \sin^2 \theta_{\text{W}})Z - N]$, where θ_{W} is the weak mixing angle, and Z and N are the number of protons and neutrons, respectively; $\rho(\mathbf{r})$ stands for the nuclear density; and the fifth gamma matrix can be written as $\gamma^5 = -i\gamma^0\gamma^1\gamma^2\gamma^3$, with Dirac matrices $\gamma^0, \gamma^1, \gamma^2, \gamma^3$. The subscript j in γ_j^5 indicates it acts on electron j . The Hamiltonian in Eq. (1) will yield a contribution to the energy that is positive for one enantiomer, and negative for the other.

In this work, we calculate the PV difference in the vibrational transition frequencies between the two enantiomers as illustrated in Fig. 1. The molecular geometries were optimized at the density functional theory (DFT) level, using an effective core potential on the central metal atom to account for scalar relativistic effects. The normal modes and corresponding frequencies were calculated in a harmonic frequency analysis; here we neglect the coupling between the vibrational modes.

Subsequently, several normal modes are selected for further fully relativistic calculations (see further below). For each chosen mode, eleven single-point relativistic DFT calculations are performed for geometries along the normal mode, yielding the PV energy contribution $V_{\text{PV}}(q)$ (as the ex-

pectation value of \hat{H}^{PV} , Eq. (1)) as a polynomial function of the normal coordinate, q .

Next, the vibrational wavefunctions $|n\rangle$ are found by solving the vibrational Schrödinger equation numerically following the Numerov–Cooley procedure, for the potential obtained along the normal mode [48–50]. Then, the shift of a vibrational level n can be calculated as

$$E_n^{\text{PV}} = \langle n | V^{\text{PV}}(q) | n \rangle. \quad (2)$$

From this we find the PV frequency difference for a transition from level m to n between the left- and right-handed form of the molecule:

$$\Delta\nu_{m \rightarrow n}^{\text{PV}} = \frac{2}{h}(E_n^{\text{PV}} - E_m^{\text{PV}}), \quad (3)$$

with h Planck’s constant, and where the factor of two arises from the fact that the energy of one enantiomer is shifted up by the PV effects, while that of the other is shifted down by the same amount.

In this work, we define the sign of this frequency difference via

$$\Delta\nu_{m \rightarrow n}^{\text{PV}} = \nu_{\Delta} - \nu_{\Lambda} = \nu_{\Delta}^{\text{PV}} - \nu_{\Lambda}^{\text{PV}} = 2\nu_{\Delta}^{\text{PV}}, \quad (4)$$

where ν_{Δ} and ν_{Λ} are the $m \rightarrow n$ transition frequencies and ν_{Δ}^{PV} and $\nu_{\Lambda}^{\text{PV}} = -\nu_{\Delta}^{\text{PV}}$ stand for the frequency shifts of these transitions in the Δ and Λ enantiomer, respectively (see Fig. 1).

Computational details. – Most of the calculations were performed for a particular set of computational parameters (basis set and DFT functional) which we refer to as the reference; to ensure the robustness and consistency of the results, these parameters were varied for a few normal modes and the results compared. More details can be found in the Supplementary Material [51].

For the geometry optimizations [52] we chose the Def2-TZVPP basis set [53, 54] and the B3LYP functional [55], with Grimme D3 dispersion [56]. Relativistic effects were included by means of the effective-core potential on the central metal atom in the calculation: ECP28MDF on ruthenium [57] and ECP60MDF on osmium [58]. Subsequent relativistic exact two-component (X2C) Hamiltonian [63] DFT calculations were performed with the DIRAC18 computational program [59]. As the reference for these calculations we take the CAM-B3LYP* functional [29], which is a Coulomb-attenuated B3LYP functional [60] with parameters optimized for reproducing PV shifts obtained at the coupled cluster level of theory. We used Dyall’s v3z basis set on the ruthenium/osmium and oxygen atoms and Dyall’s v2z basis set on the carbon and hydrogen atoms [61, 62]. Two-electron spin-same-orbit interactions are

are introduced in a mean-field fashion by the AMFI procedure [64]. The vibrational PV shifts calculated in the X2C procedure have been shown before to differ from those obtained in the full four-component framework by not more than a few percent [33].

The relativistic calculations are still demanding computationally; thus we selected a few important modes for our investigation, based on the outcome of the vibrational analysis. In order to have a large differential PV shift, the parity violating energy should vary significantly over the range of a vibration [34].

The parity violating energy scales with atomic number and thus the metal center of the complex will contribute most to the total PV energy difference. For a large change in the electronic density at the metal over the course of a vibration, we need a large change in electronic wave function in its vicinity, which can be achieved by a large change in the position of the oxygen atoms surrounding the metal center. As a measure hereof, we take the sum of the moduli of the M–O displacements along the normal mode q :

$$\sum_{i=1}^6 \sqrt{(\Delta x_{\text{M-O},i})^2 + (\Delta y_{\text{M-O},i})^2 + (\Delta z_{\text{M-O},i})^2} \quad (5)$$

where $(\Delta x_{\text{M-O},i}, \Delta y_{\text{M-O},i}, \Delta z_{\text{M-O},i})^{\text{T}} = \vec{d}_{\text{M}} - \vec{d}_{\text{O},i}$, *i.e.* the differences of the metal and i th oxygen displacement coordinates associated with normal mode q (with the corresponding displacement vectors being normalized).

Results: Ru(acac)₃. – As we could not find any high-resolution vibrational spectroscopic investigation in the literature, we synthesized grams of pure Λ and Δ enantiomers of Ru(acac)₃ (following a recipe detailed in the Supplementary Material [51]) and recorded our own Fourier transform infrared spectrum of Λ -Ru(acac)₃ trapped in solid neon at 3 K. Such low-temperature matrix-isolation measurements are not muddled by rotations, which are mostly inhibited, and exhibit narrower bands than the more traditional room-temperature studies in the liquid or solid phase. Importantly, the obtained vibrational band centres are typically shifted by only a few wavenumbers (0.3% of the transition frequency at most) with respect to the gas-phase conditions of the parity violation measurements (see details in the Supplementary Material [51]), a level of uncertainty that the current theory can simply not provide. The distributed feedback quantum cascade lasers (QCLs) that will be used in the PV measurements typically cover a few wavenumbers. Thus, this precursor spectroscopic characterisation is crucial for deciding which laser system to build. Of course, the theory-experiment comparison is also important for identifying the most suitable vibrational modes for measurements.

Fig. 2 compares the calculated frequencies resulting

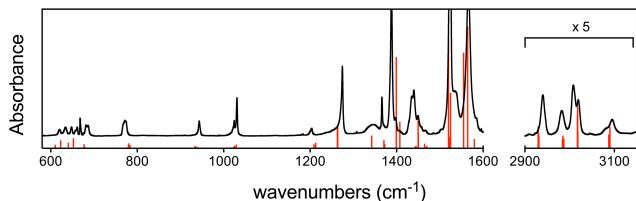


FIG. 2. Comparison between the calculated vibrational spectrum (red lines) of $\text{Ru}(\text{acac})_3$ from the geometry optimisation and the infrared Fourier transform spectrum recorded in solid neon at 3 K (above 2800 cm^{-1} intensities and absorbance have been multiplied by a factor of 5). The calculated harmonic frequencies greater (resp. smaller) than 1700 cm^{-1} have been scaled with a scaling factor of 0.964 (resp. 0.98) for comparison with the measured spectrum. The baseline of the experimental spectrum is vertically shifted for clarity.

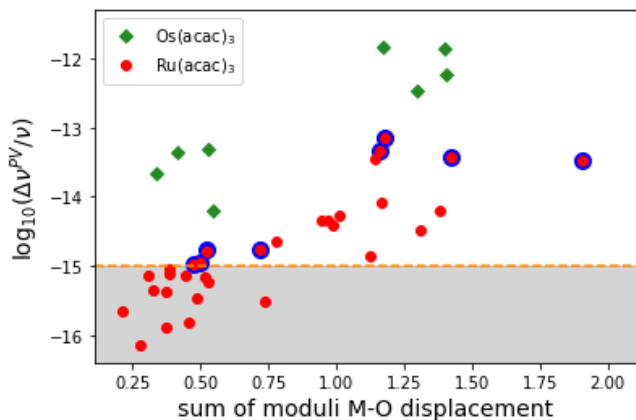


FIG. 3. Calculated relative PV frequency shifts ($\Delta\nu^{\text{PV}}/\nu$) of several vibrational transitions in $\text{Ru}(\text{acac})_3$ and $\text{Os}(\text{acac})_3$ as a function of the indicator (sum of moduli of Ru-O or Os-O displacements, see text). The red dots represent $\text{Ru}(\text{acac})_3$, with the larger dots highlighted in blue corresponding to the selected normal modes shown in Tab. I, the green diamonds represent the corresponding normal modes of $\text{Os}(\text{acac})_3$ shown in Tab. II and the orange dotted horizontal line is the expected sensitivity attainable by ultra-high resolution vibrational spectroscopy bordering the grey zone inaccessible to measurements.

from the geometry optimisation shown in the form of a stick spectrum with the matrix-isolation measurement. Overall, the calculated vibrational spectrum is in good agreement with our matrix-isolation spectrum. Details on the spectroscopy, and in particular the assignment of the observed bands to the corresponding internal modes, can be found in the Supplementary Material [51].

The calculated PV shifts are plotted against the indicator of the M-O displacement in Fig. 3 for $\text{Ru}(\text{acac})_3$. A clear correlation between the magnitude of the displacement and the size of the calculated PV shift can be observed. This correlation can assist in selecting viable normal modes for calculation in similar compounds.

In addition to the magnitude of the PV frequency

shifts, a number of experimental considerations are to be taken into account when selecting the vibrational modes for measurements. The intensity of the selected mode should be high enough to make the measurement feasible and its frequency should lie in a range accessible to current laser technologies. The group at LPL in Paris that is currently working on $\text{Ru}(\text{acac})_3$ has CO_2 lasers [65] and quantum cascade lasers (QCLs) [24, 66–68] of record frequency stabilities and accuracies necessary for measuring the tiniest PV frequency differences. CO_2 lasers, until recently the only available stable sources for precise mid-infrared spectroscopy, span the 9–11 μm range. Continuous-wave (cw) QCLs are commercially available in the 4–13 μm range and more sporadically up to 17 μm . The LPL group has several cw QCLs between 10 and 11 μm ($910\text{--}980 \text{ cm}^{-1}$ range) and one of the few existing QCLs emitting at 17.2 μm made by R. Teissier and co-workers [69].

Based on the above criteria (both in terms of a large predicted PV shift and the desired wavelength range) we display a number of promising normal modes in Tab. I. All these modes have a relative PV frequency shift $\Delta\nu^{\text{PV}}/\nu$ of 10^{-15} or above, which is the sensitivity aimed for in the LPL experiment. For comparison, the PV shift of CHFClBr , a molecule on which much of the experimental work has been conducted so far, has a predicted $\Delta\nu^{\text{PV}}/\nu \approx -8 \times 10^{-17}$ [27, 28].

Particularly interesting for the experiment are thus normal modes 52 and 53 as they are in the laser window currently available at LPL, are reasonably infrared active, and have a predicted PV shift on the 10^{-15} level. The C-O stretch vibrational modes 100 and 102 look even more promising, given their remarkably high intensity, their twice higher predicted relative PV shift, and the commercial availability of QCLs in the corresponding spectral window. Finally, normal modes 17, 19, 20 and 29 should not be overlooked, not only because of their record 10^{-14} relative predicted shift, but also because of their lower frequencies, which may prevent the onset of intramolecular vibrational energy redistribution that could obscure the spectra at higher frequencies. However, proper radiation sources are still unavailable in this spectral window.

Results: $\text{Os}(\text{acac})_3$. – We compared our calculated frequencies for $\text{Os}(\text{acac})_3$ with the vibrational spectrum recorded by Dallmann and Preetz [46], and found a good agreement. Details on this comparison can be found in the Supplementary Material [51].

For $\text{Os}(\text{acac})_3$, calculations were performed for the normal modes that correspond to those of $\text{Ru}(\text{acac})_3$ displayed in Tab. I. In order to identify the corresponding vibrational modes of the two molecules, we take their overlap ϕ , calculated as the normalized dot product of normal coordinates. For the corresponding normal modes, ϕ should approach 1. In this comparison, we found it sufficient to take into account only the displacements of the central metal and the surrounding oxygens (which are the most relevant for the PV shift). The over-

normal mode	ν [cm ⁻¹]	IR int. [km/mol]	$\Delta\nu^{\text{PV}}$ [mHz]	$\frac{ \Delta\nu^{\text{PV}} }{\nu}$
17	182	0.009	-449	7.2×10^{-14}
19	201	1.718	-298	4.6×10^{-14}
20	223	0.065	279	3.8×10^{-14}
29	327	7.884	325	3.4×10^{-14}
52	953	9.564	-30	1.0×10^{-15}
53	954	1.793	-33	1.1×10^{-15}
100	1586	453.5	-83	1.7×10^{-15}
102	1612	44.22	-111	2.3×10^{-15}

TABLE I. Summary of the Ru(acac)₃ theoretical results: promising normal modes with either particularly large predicted vibrational shifts on the 10⁻¹⁴ level (modes 17-29), or a large shift in combination with a frequency in the range of current laser systems (modes 52 and 53), or very large infrared intensity (IR int.) (modes 100 and 102). The vibrational frequencies (ν) shown are the harmonic frequencies obtained from the frequency analysis.

lap ϕ is normalized by dividing by the geometric mean of the respective displacement vector moduli as:

$$\phi = \frac{\sum_i^{M,\text{O}} \vec{d}_{i,\text{Ru}(\text{acac})_3} \cdot \vec{d}_{i,\text{Os}(\text{acac})_3}}{\sqrt{\sum_i^{\text{Ru},\text{O}} |\vec{d}_{i,\text{Ru}(\text{acac})_3}|^2 \sum_i^{\text{Os},\text{O}} |\vec{d}_{i,\text{Os}(\text{acac})_3}|^2}} \quad (6)$$

Here, $\vec{d}_{i,X}$ denotes the displacement vector of atom i in complex X , and M the metal center of the complex in question.

The results of the PV calculations for Os(acac)₃ are presented in Tab. II and in Fig. 3. For all of the normal modes, the signs of the PV shifts are the same for the Ru and the Os complexes. This shows that the two molecules behave in a similar way, and emphasizes the similarity of the vibrational modes between the complexes and the robustness of the PV shift under slight geometric changes. A striking observation is that the relative PV shifts $|\Delta\nu^{\text{PV}}/\nu|$ in Os(acac)₃ are more than an order of magnitude larger than those in Ru(acac)₃, reaching 10⁻¹² levels. A closer look at the ratio of absolute shifts (which is similar to the ratio of relative shifts as the transition frequencies do not vary drastically between Ru(acac)₃ and Os(acac)₃) reveals, for some of the transitions, a significant enhancement beyond the Z^5 scaling, which would amount to $\Delta\nu_{\text{Os}(\text{acac})_3}^{\text{PV}}/\Delta\nu_{\text{Ru}(\text{acac})_3}^{\text{PV}} \approx 15.4$. This is not entirely unexpected, as the Z^5 dependence was derived for the absolute PV energy shifts [37] rather than for vibrational transitions; furthermore, similar beyond-the- Z^5 scaling was observed in chiral uranium compounds by Wormit *et al.* [34].

Here, it has very favourable consequences for the experiment; the two transitions in Tab. II that lie in the laser window currently available at LPL (modes 52 and 53) experience an enhancement of a factor of 48 and 40, respectively, when changing from Ru(acac)₃ to Os(acac)₃, significantly larger than the Z^5 scaling used for a rough estimate would predict. This enhancement

pushes the $|\Delta\nu^{\text{PV}}/\nu|$ of these modes into the $\sim 10^{-12}$ regime, making it much easier to detect at the level of sensitivity already demonstrated at LPL [22, 70]. This finding provides us with a strong motivation to synthesize this compound and bring it into the gas phase.

Conclusions. – In this work, we have calculated the PV vibrational frequency shifts for a selection of normal modes in Ru(acac)₃, a robust, readily available and promising candidate for the first detection of parity violation in molecules. We have demonstrated that the results are computationally robust and have derived a simple scheme for identifying the most promising vibrational modes based on the displacement of the atoms within the transition. A number of transitions with exceptionally large PV shifts of hundreds of mHz (corresponding to relative frequency shifts on the order of 10⁻¹⁴) were identified. Other transitions that lie in the spectral range of laser systems currently achievable at LPL, where the experiment is being built, are predicted to have fractional PV shifts on the order of 10⁻¹⁵. This is around the sensitivity that is aimed for by the group at LPL, and one to two orders of magnitude larger than that of CHFClBr, the molecule on which previous PV measurements were conducted. Preliminary spectroscopic investigations of some of the promising vibrational modes conducted in solid neon at 3 K show good agreement with our calculations.

Furthermore, the scaling of the vibrational PV shifts with atomic number Z was investigated by comparison with Os(acac)₃, where osmium is the heavier homologue of ruthenium. Here, we find enhancements of the PV shifts that exceed the prediction following from the naive Z^5 scaling; this is in accordance with earlier findings [34]. This is especially auspicious for the experiment: the investigated modes that fall in the accessible laser windows are enhanced to the 10⁻¹² fractional shift regime, making detection feasible. Os(acac)₃ can be synthesised [46], and the next experimental steps are to investigate its stability upon heating for bringing it into the gas phase for the high-resolution spectroscopic studies, and its enantiomeric resolution. Moreover, ⁹⁹Ru, ¹⁰¹Ru, ¹⁸⁷Os and ¹⁸⁹Os nuclei are NMR active and thus the Ru(acac)₃ and Os(acac)₃ complexes potentially open up a possibility for gas phase NMR measurements.

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mode(Os)	ν [cm ⁻¹]	IR int. [km/mol]	$\Delta\nu^{\text{PV}}$ [Hz]	$\frac{\Delta\nu^{\text{PV}}}{\nu}$	mode(Ru)	ϕ	$\frac{\Delta\nu^{\text{PV}}(\text{Os})}{\Delta\nu^{\text{PV}}(\text{Ru})}$
16	191	0.091	-9.72	1.5×10^{-12}	17	0.996	21.7
19	211	2.356	-9.59	1.4×10^{-12}	19	0.961	32.2
20	224	0.013	4.30	5.9×10^{-13}	20	0.948	15.4
29	308	2.392	3.09	3.4×10^{-13}	29	0.838	9.5
52	952	0.464	-1.47	5.0×10^{-14}	52	0.830	48.4
53	954	1.272	-1.32	4.5×10^{-14}	53	0.831	40.1
100	1563	245.6	-1.04	2.2×10^{-14}	100	0.955	12.7
102	1589	102.2	-0.31	6.3×10^{-15}	102	0.985	3.6

TABLE II. The PV shift of vibrational normal modes in Os(acac)₃ and a comparison to Ru(acac)₃. Normal modes in the two compounds were matched to each other according to their overlap ϕ as defined in Eq. 6. IR int. stands for infrared intensity. The vibrational frequencies (ν) shown are the harmonic frequencies obtained from the frequency analysis.

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