Long rotational coherence times of molecules in a magnetic trap: Supplemental Material

L. Caldwell,[1] H. J. Williams,[1] N. J. Fitch,[1] J. Aldegunde,[2] Jeremy M. Hutson,[3] B. E. Sauer,[1] and M. R. Tarbutt[1]

[1] *Centre for Cold Matter, Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2AZ UK*
[2] *Departamento de Quimica Fisica, Universidad de Salamanca, E-37008, Salamanca, Spain*
[3] *Joint Quantum Centre (JQC) Durham-Newcastle, Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK*

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I. ELECTRONIC STRUCTURE CALCULATIONS OF g_r AND g_l

We calculate g_l, the anisotropy of the electronic g tensor, using density functional theory (DFT) with the B3LYP functional [26]. This functional was chosen because, as discussed in reference [42], it is better than other functionals at reproducing experimental values of g_l and γ; the latter characterizes the electron spin-rotation interaction and is connected to g_l via Curl's approximation [43]. The calculations include relativistic corrections via the zero-order regular approximation (ZORA) [28–30] and are performed with the ORCA code [25]. Experimental values of g_l are available for numerous $^2\Sigma$ molecules, including most of those discussed in Table I [44–54]. In general, our calculations agree with experimental values within 5%, although the difference may increase up to 20% when comparing with measurements performed in noble-gas matrices or when the value of g_l is not directly measured but is extracted from γ using Curl's approximation, which is known to introduce an error around 15% [55]. Such larger discrepancies occur, for example, for MgOH (measured in a matrix [52]) and CaH (g_l obtained from γ [49]).

We are unable to use the same methodology for the rotational g factor, g_r, because its calculation is not supported by ORCA. As correlation effects are relatively small for g_r [56], we calculate it using Hartree-Fock (HF) calculations performed with the DALTON code [31]. Unfortunately, very few experimental values of g_r are available for open-shell molecules and, in particular, for those included in Table I. The only exception to this is CaF, for which the calculated value is in good agreement with the experimental value obtained in the present work, $g_r = -5.0(2) \times 10^{-5}$.

We initially attempted to perform calculations on Yb as well as the lighter metals in Table I, but ultimately decided they were not reliable enough for publication. To provide consistency across all the elements, we chose to use the x2c-TZVPP basis sets of Pollak and Weigend [27] for both DFT and HF calculations. These basis sets are of triple-ζ quality, and are designed for use in relativistic calculations. They are available for all atoms in the periodic table up to Rn.

The DFT and HF methods we use here are reliable only for molecules that are reasonably well described by a single electron configuration. In order to verify this, we performed CCSD(T) calculations and used the T1 diagnostic [57] to assess the multiconfigurational character of the ground electronic state. A value T1 > 0.02 is generally considered to indicate that multireference calculations are needed. For the molecules in Table I, T1 was below this threshold, indicating that the ground state is reasonably well described by a single configuration.

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