Introduction. Cold molecules are currently heavily studied and serve as particularly interesting targets for spectroscopy \[1\]. A wealth of applications of cold molecular systems for high-precision spectroscopy \[2\], including the search for violation of fundamental symmetries \[3, 4\] and variation of fundamental constants \[5\] as well as controlled cold chemistry \[6\], quantum computations (see e.g. review \[7\]) and many others, have been considered recently. Among popular techniques for obtaining samples of cold and ultra-cold molecules are photoassociation from cold atoms \[8\]. Stark deceleration of the molecular beams \[9\] and cooling with buffer-gas \[10\]. Recently, considerable progress has been reported for direct Doppler cooling of diatomic molecules with lasers \[11, 12\]. The latter method looks especially promising, as it is intimately connected with well-developed techniques for cooling and trapping atoms. Thus, in principle, diverse advances in atomic Doppler cooling can be transferred to the related schemes for molecules. For example the magneto-optical trapping widely used with cold atoms was recently demonstrated for magneto-optical trapping of YO \[12\] and SrF \[13\].

As of yet, however, only diatomic molecules could successfully be Doppler cooled with lasers as molecules amenable for Doppler cooling must feature Franck–Condon (FC) factors close to unity for transition between those vibronic states involved in the closed transition cycles (usually the ground and first excited electronic state). Peculiarities of the electronic structure in systems possessing quasi-diagonal FC matrices have been identified in Ref. \[3\]. Almost parallel Born–Oppenheimer potential energy curves of the electronic ground and excited state (which results in diagonality of the FC matrix) are expected in diatomic molecules with one valence electron over closed shells, when essentially this electron undergoes transition between non-bonding orbitals upon electronic excitation.

We pointed out \[14\] that in polyatomic molecules with a valence electron undergoing transitions between non-bonding orbitals quasi-closed transition loops should also be present, which opens up an avenue to cold samples of larger molecules. In this Letter we provide examples of polyatomic molecules which are expected to have quasi-diagonal FC matrices for vibronic transitions between electronic states and are thus potentially amenable for direct cooling with lasers. Classes of molecules and explicit examples together with possible routes for generating proper molecular structures were originally reported on the Conference for Cold and Controlled Molecules and Ions (Monte Verità (Switzerland), 2014).

Common consideration. A straightforward way to identify polyatomic molecules with electronic properties similar to those of diatomic molecules is to apply substitution: e.g. in the series of MF open-shell diatomic molecules (class I molecules \[3\]), where M is the metal from the group 2 of Periodic Table (Be–Ra), one can substitute fluorine for a pseudohalogenic group such as CN, NC, SCN or functional groups such as OH or CH\(_3\). It can be expected from simple theoretical concepts that the leading electronic configurations for ground and excited states of the resulting compounds differ only by the state of the valence electron, which occupies either lowest (for ground state) or next by energy (for excited state) non-bonding orbital, similar to the original MF molecule. For above-mentioned compounds we also benefit from the fact that the respective non-bonding orbitals are mainly centred on metal atom with their centre-of-mass shifted away from the bonding region (see Fig. 1). Of course, the analogous scheme can be applied to class II molecules (e.g. in HI\(_2^+\) cation one can change H to OH or NC group etc). We emphasize, though, that even in the case of valence electron undergoing transition between non-bonding orbitals the quasidiagonality of FC matrix can be expected, but not guaranteed. Counteracting are, for instance, the Renner–Teller or Jahn–Teller effects, which are absent for diatomic molecules, but can considerably influence the equilibrium structure and vibrational frequencies of polyatomic molecules. For example, for the molecule MgOH the equilibrium structure of the ground state is linear, whereas the one of the excited state is bent \[15\], so quasi-diagonal FC matrix can hardly be expected in this case. Typically, FC factors are extremely sensitive to relative displacements in equilibrium distances of the electronic states, thus even estimates of large FC factors (bigger than 0.5) with high accuracy is challenging. Thus, the simple theoretical concepts primarily provide guidelines, whereas modern quantum chemical approaches are required to narrow down the initial selection of the candidates.

Linear triatomic molecules. Examples of linear molecules, for which quasidiagonal FC matrices can be expected, are calcium monohydroxide (CaOH) and calcium monoisocyanide (CaNC). CaOH and CaNC have the advantage of featuring a linear equilibrium
structure in the ground and essentially also in the lowest excited doublet state, thus allowing direct adaptation of the cooling scheme used for diatomic molecules. Besides, CaNC possesses a large electric dipole moment (about 6 Debye, see Table I), which renders this molecule especially attractive for the combined scheme of Stark deceleration and subsequent (or simultaneous) laser cooling. We calculated molecular parameters and FC factors for vibronic transitions between ground and excited electronic states. The results are summarised in the Table I.

**Computational details:** Input files for calculations and additional data are provided in the Supplementary materials. The MOLPRO program package [16] was used for electronic structure calculations. Subsequent computation of FC factors in the harmonic approximation were performed with our hotFCHT code [17–19]. Basis sets of quadruple-zeta or triple-zeta quality augmented with polarisation valence basis functions (def2-QZVPP and def2-TZVP) are used for all atoms. All electronic structure calculations start with the closed-shell Hartree-Fock calculations of the ground-state configuration of the singly charged molecular cation to obtain initial guess for molecular orbitals. Then calculations in the framework of complete active space self-consistent field (CASSCF, [20]) were performed, followed by configuration interaction (CI, [21]) calculations.

The FC factors for transitions between the ground vibrational state of the first electronically excited state and all vibrational states of the electronic ground state is estimated in all cases. A few calculations with different level of accounting for electronic correlations and basis sets were used to check the stability of the computed FC factors. Details of the calculations can be found in the supplementary material. We emphasize that in all cases the sum of three largest FC factors is always larger than 0.9 for both CaNC and CaOH, that clearly indicates the potential of these molecules (and, although with exceptions, the general class MOH and MNC, where M is an alkaline earth metal Be-Ra) for direct cooling with lasers.

**Non-linear polyatomic molecules** Examples of non-linear polyatomic molecules having a valence electron on non-bonding orbitals are CaCH$_3$ and MgCH$_3$. The scheme of arriving at these molecules is analogous to the one in the previous paragraph, with the obvious difference in the pseudohalogenic group by methyl. Both molecules have essentially diagonal FC matrix for transitions between ground and first excited electronic state (see Table I). The important feature of these molecules is a quite small Jahn-Teller effect (see the data of the experimental measurements of Jahn-Teller parameters in [22] for MgCH$_3$), which also favours quasi-diagonal FC matrix. The computational scheme was essentially analogous to the one used for CaOH and CaNC (same basis sets, calculations of the closed-shell cation at first stage followed by MCSCF and CI calculations, see supplementary material). As making detailed/high-precision electronic structure calculations is out of the scope of the current paper we used a simplified scheme by considering only the totally-symmetric modes (C$_{3v}$ molecular symmetry group) in calculations of FC factors rather than solving the full vibronic coupling problem. To check the influence of the non-totally symmetric modes, calculations for MgCH$_3$ were performed without symmetry restrictions and then FC factors were calculated in the harmonic approximation. As one can see from Table I the calculated molecular parameters are in good agreement with the experimental measurements and sum of FC factors for three vibration modes with largest FC factors is higher than 0.8 for MgCH$_3$ even when non-totally symmetric modes are accounted for. Besides, the quite large dipole moment of CaCH$_3$ indicates its potential for Stark deceleration.

**Chiral molecules** Cooling and trapping of chiral molecules would mean a crucial improvement in accuracy for spectroscopic measurements of a number of highly interesting effects e.g. parity violating energy differences between enantiomers due to the fundamental weak interaction [23][24]. Using the scheme from the above paragraphs it is also possible to identify chiral molecular structures having quasidiagonal FC matrix. One way is isotopic substitution to a known molecule [23][24]. We calculated FC factors for the molecule MgCHDT, using the same method for electronic structure calculation as in the case of MgCH$_3$, without accounting for molecular symmetry. The resulting FC factors we obtained are the following: (0.6404, 0.1792, 0.03979) with $\sum$ equal 0.8594. Thus FC factors are predicted to be only slightly smaller than for MgCH$_3$. This finding is excellent news for attempts to obtain (ultra)cold chiral molecules for the search of violation of fundamental symmetries.

**Conclusions** We have outlined a rational approach to identify polyatomic molecules that appear to be promising candidates for direct Doppler cooling with lasers. Explicit numerical calculations for structures and Franck-Condon factors of selected representatives indicates high potential for laser-cooling of such molecules for even opening up the third spatial dimension for ultracold molecules generated by direct Doppler cooling with lasers.

We are very grateful to organisers (Christiane Koch and Andreas Osterwalder) and participants of the Conference for Cold and Controlled Molecules and Ions (Monte Verità (Switzerland), 2014) for fruitful discussions and critical remarks. In particular we thank Ronnie Kozloff, who attracted our attention to CaNC molecule. Hauke Westemeier is acknowledged for creating the figure with the molecular orbitals.
TABLE I. Calculated and experimental molecular parameters and FC factors for CaOH and CaNC. For CaOH the results of the calculations which best reproduce the experimental internuclear distance $R_{(\text{Ca-O})}$ is presented (MCSCF/def2-QZVPP). For CaNC the results of MCSCF calculations with the def2-QZVPP basis set is given. See also the next section for discussion on stability/accuracy of FC factors and supplementary materials for additional data. Internuclear distances $R_i$ are given in Å, electric dipole moments in Debye, transition wavenumbers $T_e$ and normal vibrational wavenumbers $\nu_l$ in inverse centimeters. For FC factors vibrational quantum numbers are given with the corresponding overtones, e.g $3^{(0)}$ is FC factor for vibronic transition between ground (0) vibrational state of the excited electronic state and vibrational state with the third doubly excited vibrational mode (bending mode) of the ground electronic state. The irreducible representation $e$ is two-dimensional, but the degeneracy slightly lifted in the numerical calculations. Thus, we provide vibrational wavenumbers of both components.

| State | CaOH | | | CaNC | | |
|-------|------|---|---|------|---|---|
|       | Calculation | Experiment |     | Calculation | Experiment |     |
| X ($^2\Sigma$) | $R_{(\text{Ca-O})}$ | 2.0038 | 1.9746 | $R_{(\text{Ca-N})}$ | 2.2344 | 2.2065 |
|       | $R_{(\text{O-H})}$ | 0.9333 | 0.9562 | $R_{(\text{N-C})}$ | 1.1866 | 1.1186 |
|       | $\angle \text{Ca-O-H}$ | 179.97 | 180.00 | $\angle \text{Ca-N-C}$ | 179.54 | 180.00 |
|       | $|D|$ | 0.45 | 1.465 | $|D|$ | 6.08 | 6.84 |
| A ($^2\Pi$) | $R_{(\text{Ca-O})}$ | 1.9769 | 1.9532 | $R_{(\text{Ca-N})}$ | 2.2076 |  |
|       | $R_{(\text{Ca-O})}$ | 0.9332 | 0.9572 | $R_{(\text{N-C})}$ | 1.1861 |  |
|       | $\angle \text{Ca-O-H}$ | 179.97 | 180.00 | $\angle \text{Ca-N-C}$ | 179.97 |  |
|       | $|D|$ | 0.25 | 0.836 | $|D|$ | 5.91 |  |
|       | $T_e$ | $15 \times 10^3$ | $T_e$ | $16 \times 10^3$ |     |     |
| FC factors | 0.9993 | 0.0004 | 0.00017 | FC factors | 0.9092 | 0.0715 | 0.0056 |
| $\sum$ | > 0.999 |     |     | $\sum$ | 0.9864 |     |     |

| Normal modes $\nu_l$ | | | Normal modes $\nu_l$ | | |
| X ($^2\Sigma$) | $\nu_1(a_1)$ | 4276 | $\nu_1(a_1)$ | 2062 |
|       | $\nu_2(a_1)$ | 622 | $\nu_2(a_1)$ | 412 |
|       | $\nu_3(e)$ | 411/408 | $\nu_3(e)$ | 85/85 |
| A ($^2\Pi$) | $\nu_1(a_1)$ | 4279 | $\nu_1(a_1)$ | 2066 |
|       | $\nu_2(a_1)$ | 646 | $\nu_2(a_1)$ | 426 |
|       | $\nu_3(e)$ | 402/386 | $\nu_3(e)$ | 63/63 |

\[a\] from [26]  
\[b\] from [27], only data for X state are available  
\[c\] in previous investigation in [26] the calculated electric dipole moment for X state is also considerably smaller than experimentally measured, the reason for such a big discrepancy probably connected with the compensation of the large dipole moment form the ionic core by charge distribution from the valence electron  
\[d\] from [29]  
\[e\] from [29]  
\[f\] bending mode  
\[g\] Ca–OH stretching  
\[h\] Ca–NC stretching  
\[i\] 2(0) bending mode  
\[j\] 3(2) bending mode
| State         | Calculation | Experiment | State         | Calculation | Experiment |
|---------------|-------------|------------|---------------|-------------|------------|
| X ($^{2}A_1$) | 2.1204(2.1205) 2.102 | X ($^{2}A_1$) | R(Ca−C) 2.4206 2.349 |
| R(Mg−C)      | 1.0932(1.0931) 1.105 | R(Ca−H) 1.1095 1.100 |
| R(C−H1)      | 1.0932(1.0931) 1.105 | | |
| R(C−H2)      | 1.0932(1.0931) 1.105 | | |
| R(C−H3)      | 1.0932(1.0931) 1.105 | | |
| | 0.91 (0.91) 0.76 | |
| X ($^{2}E$)  | 2.1636(2.1629) 2.124 | A ($^{2}E$) | R(Ca−C) 2.4052 − |
| R(Mg−C)      | 1.085(1.084) 1.105 | R(Ca−H) 1.0892 − |
| R(C−H1)      | 1.085(1.084) 1.105 | | |
| R(C−H2)      | 1.085(1.087) 1.105 | | |
| R(C−H3)      | 1.085(1.087) 1.105 | | |
| | 0.92 (0.93) − | |
| T_e          | 14×10^3 | T_e |
| FC factors   | 0.7090 (0.6714) | 0.19218(0.1728) |
| ∑            | 0.02635 (0.03271) | |
| A ($^{2}E$)  | 2.69(0) | A ($^{2}E$) | ν_1(a_1) 2863 |
| ν_1(a_1)     | 2605 | ν_1(a_1) | 1187 |
| ν_2(a_1)     | 1089 | ν_2(a_1) | 418 |
| ν_3(a_1)     | 443 | ν_3(a_1) | 435 |

| State         | Calculation | Experiment | State         | Calculation | Experiment |
|---------------|-------------|------------|---------------|-------------|------------|
| X ($^{2}A_1$) | 3043        | X ($^{2}A_1$) | ν_1(a_1) 3035 |
| ν_1(a_1)     | 1154        | ν_2(a_1)   | 1187 |
| ν_2(a_1)     | 511         | ν_3(a_1)   | 418 |
| A ($^{2}E$)  | 2605        | A ($^{2}E$) | ν_1(a_1) 2863 |
| ν_1(a_1)     | 2605        | ν_1(a_1)   | 1187 |
| ν_2(a_1)     | 1089        | ν_2(a_1)   | 418 |
| ν_3(a_1)     | 443         | ν_3(a_1)   | 435 |

a MCSCF/Ci calculation in C_3v symmetry, results without accounting for symmetry (including non-symmetrical modes in FC factors) are in parenthesis
b from [30]
c MCSCF calculations in C_3v symmetry
d from [31]
e in [30] this value is fixed from theoretical calculations by G.Gawboy
f prediction from [32]
g 0(0) 
h 3(1) 6(0) umbrella mode
i 0(0)
j 2(0) Ca−CH_3 stretching mode
k 3(1) umbrella mode
l 2(1) 3(0) (0(2)) stretching Mg−CH_3 + umbrella modes
FIG. 1. Isosurfaces of the non-bonding orbitals for CaCH$_3$ molecule. The single occupied molecular orbital (SOMO) for ground electronic configuration is in solid color (blue for both positive and negative signs of one-electron wavefunction, iso value is 0.055 $a_0^{-3/2}$), whereas the SOMO for excited state configuration is in transparent light-yellow color (iso value is 0.040 $a_0^{-3/2}$). It is seen that electronic densities are shifted outside of the bonding region and that ground-state SOMO is s–p hybridised, while excited state SOMO is rather p–d hybridised.

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