## Polyatomic Candidates for Cooling of Molecules with Lasers from Simple Theoretical Concepts

Timur A. Isaev<sup>\*</sup> and Robert Berger

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str 4, Marburg 35032, Germany (Received 15 May 2015; published 12 February 2016)

A rational approach to identify polyatomic molecules that appear to be promising candidates for direct Doppler cooling with lasers is outlined. First-principles calculations for equilibrium structures and Franck-Condon factors of selected representatives with different point-group symmetries (including the chiral nonsymmetric  $C_1$ ) have been performed and a high potential for laser cooling of these molecules is indicated.

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Introduction.-Cold molecules are currently heavily studied and serve as particularly interesting targets for spectroscopy [1,2]. A wealth of applications of cold molecular systems for searching violations of fundamental symmetries [3,4], dark matter [5], and variations of fundamental constants [6], as well as for exploring controlled chemistry [7], quantum computations (see, e.g., review [8]), and many others, have been considered recently. A special issue of Chemical Reviews [2] contains comprehensive reviews of some popular techniques for obtaining samples of cold and ultracold molecules, among which are photoassociation from cold atoms, Stark and Zeeman deceleration of the molecular beams, and buffergas cooling. Presently, the stimulated Raman adiabatic passage (STIRAP) technique used to transfer Feshbach molecules to the rovibronic ground state provides the lowest temperatures and highest densities of diatomic molecular gases (see, e.g., Ref. [9] and recent developments in Refs. [10,11]).

Considerable progress has been reported for direct Doppler cooling of diatomic molecules with lasers [12,13]. The latter method looks especially promising, as it is intimately connected with well-developed techniques for cooling and trapping of 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 YO [13] and SrF [14].

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). This is connected with the fact that Doppler cooling requires absorption and reemission of thousands to millions of photons per atom or molecule involved in cooling. The reemission process creates a dissipative force for species counterpropagating the laser beam, whereas working levels for those species copropagating the laser beam are shifted out of resonance because of the Doppler effect. Thus, closure of the cooling transition is crucial for Doppler cooling. In general, such closed transitions do not exist in molecules due to nonselective spontaneous decay from the selected rovibronic level of the excited electronic state to a multitude of rovibrational levels of the electronic ground state. The probability of such a process is proportional to the FC factor between the corresponding vibrational levels. As it was first displayed by DiRosa in 2004 [15], there exist diatomic molecules with the sum of a few largest FC factors (for transitions originating from a given vibrational level of the excited electronic state) being very close to unity. Peculiarities of the electronic structure in systems possessing such quasidiagonal 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 (mainly) nonbonding orbitals upon electronic excitation. As electronic transition between nonbonding orbitals influences the chemical bonds (formed by electrons on bonding orbitals) typically only weakly, the internuclear potential stays practically unchanged for ground and excited electronic states. The influence of the nonbonding electron is even smaller, when due to, e.g., destructive s-p hybridization the electron is shifted away from the bonding region (see next section).

We pointed out [16] that also in polyatomic molecules with a valence electron undergoing transitions between nonbonding orbitals quasiclosed transition loops should be present, which opens up an avenue to cold samples of larger molecules. In this Letter we provide examples of polyatomic molecules that may be expected to have quasidiagonal FC matrices for vibronic transitions between electronic states and are thus potentially amenable for direct cooling with lasers.

General 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, see Ref. [3] and below in this section), where M is a metal atom from group 2 of the periodic table (Be-Ra), one can substitute fluorine for a pseudohalogen such as CN, NC, SCN or functional groups such as OH or CH<sub>3</sub>. The pseudohalogens are polyatomic functional groups whose chemical properties resembles those of halogens. Particularly, the bonding situation in molecules containing pseudohalogenic groups is close to their halogen analogs, a fact known in chemistry for almost a century (see, e.g., Ref. [17]). From the electronic structure point of view one might expect that the occupation pattern of the leading electronic configurations for the ground and energetically lowest excited state of the resulting compounds differs only for the unpaired electron, which occupies then different (essentially) nonbonding orbitals, similar to the original MF molecule (see also Ref. [18] for a more detailed discussion on the expected structure for calcium derivatives). For some of the above-mentioned compounds we also benefit from the fact that the respective nonbonding orbitals are mainly centered on the metal atom with their center-of-charge shifted away from the bonding region (see Fig. 1). Of course, an analogous scheme can be applied to class II molecules. The classification of molecules according to Ref. [3] is based on electronic structure arguments. Class I molecules have nonbonding orbitals that appear due



FIG. 1. Surfaces of constant value (isosurfaces) of the nonbonding one-electron wave functions (orbitals) of the valence electron for CaCH<sub>3</sub>. The singly occupied molecular orbital (SOMO) for the ground electronic configuration is in solid color (light-blue for positive and dark-blue for negative signs of the orbital; the iso value is  $0.055 a_0^{-3/2}$ ), whereas the SOMO for the excited state configuration is in transparent yellow color (lightyellow for positive and dark-yellow for negative signs of the orbital; the iso value is  $0.040 a_0^{-3/2}$ ). It is seen that the electronic center of charges are shifted outside of the bonding region and that the ground-state SOMO is mainly a mixture of *s* and *p* wave functions centered on a Ca nucleus (*s*-*p*-hybridized orbital), whereas the excited state SOMO is rather *p*-*d* hybridized.

to interference (hybridization) of atomic valence oneelectron wave functions (e.g., s-p or p-d hybridization as shown in Fig. 1). Nonbonding orbitals in Class II molecules appear due to symmetry reasons, like in the molecular ion [19]. We emphasize, however,  $HI^+$ that even in the case of a valence electron undergoing a transition between nonbonding orbitals, quasidiagonality of the FC matrix can only 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 electronic ground state is linear, whereas the one of the energetically lowest electronically excited state is bent [20], so that a quasidiagonal 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. Calculation of FC factors with an accuracy required for a reliable prediction of laser coolability is challenging already for diatomic molecules. Nevertheless, even a 10% accuracy in calculations of FC factors, which can be conventionally reached in modern quantum chemical approaches for large (bigger than 0.5) FC factors, allows us to considerably narrow down the initial selection of candidates, whereas simple theoretical concepts primarily provide guidelines for deducing molecular candidates.

Linear triatomic molecules.- Examples of linear molecules, for which quasidiagonal FC matrices may 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 energetically 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 D, see Table I in the Supplemental Material [21]), 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 summarized in the Table I in Ref. [21], whereas FC factors together with vibrational levels are graphically represented in Fig. 2. We considered the three largest FC factors as a typical cooling experiment of diatomic molecules suggests one main pump transition and two repumpers as, e.g., in Ref. [12]. To estimate the Doppler temperature for both CaOH and CaNC we calculated the natural fluorescence lifetime  $\tau$  of the excited states (see Table III in Ref. [21]). Taking  $\tau$  to be approximately equal to 20 ns, we obtain a Doppler temperature  $T_D$  for both CaOH and CaNC according to the formula  $T_D = \hbar/(2k_B\tau)$ , where  $k_B$  is the Boltzman constant and  $\hbar = h/(2\pi)$  the reduced Planck constant.  $T_D$  is then about 1 mK, which is



FIG. 2. Schematic graphical representation of the vibronic transitions with largest FC factors for CaNC and CaOH molecules. On coordinate axes the normal coordinates  $Q_1$  and  $Q_2$  are shown for both the ground and excited electronic states.  $Q_1$  corresponds mainly to Ca-X stretching  $\Delta R = R - R_e$ , where X = OH, NC,  $R_e$  is the equilibrium distance Ca-X from Table I in Ref. [21]. Coordinate  $Q_2$  is approximately equal to  $\theta$ - $\theta_e$ , where  $\theta$  is the bending angle and  $\theta_e$  is its equilibrium value according to Table I in Ref. [21]. The approximate displacement vectors for Ca and the CN and OH groups are shown next to the corresponding coordinate axes. All parameters, including the energy E, are in arbitrary units (for the sake of clearer representation). On both plots the vibrational quantum numbers and overtones are shown next to the corresponding arrows, e.g.,  $1_2^0$  denotes the vibronic transition between the ground (0) vibrational state of the excited electronic state and the vibrational state with the first mode (1) (Ca-X stretching mode) being doubly excited (2) in the ground electronic state.

considerably lower than the typical temperature that can be reached in the framework of, e.g., buffer-gas cooling.

*Computational details.*—Input files for calculations and additional data are also provided in the Supplemental Material [21]. The MOLPRO program package [31] was used for electronic structure calculations. Subsequent computation of FC factors in the harmonic approximation were performed with our hotFCHT code [32–34]. Basis sets of quadruple-zeta or triple-zeta quality augmented with polarization valence basis functions (def2-QZVPP and def2-TZVP) were used for all atoms. All electronic structure calculations started with the closed-shell Hartree-Fock calculations of the ground-state configuration of the singly charged molecular cation to obtain an initial guess for the

molecular orbitals. Then, calculations in the framework of complete active space self-consistent field (CASSCF, [35]) were performed for the neutral molecule, followed by configuration interaction (CI, [22]) calculations. The FC factors for transitions between the ground vibrational state of the first electronically excited state and vibrational states of the electronic ground state are estimated in all cases. A few calculations with a 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 Ref. [21]. We emphasize that in all cases the sum of three largest FC factors is always larger than 0.9 for both CaNC and CaOH. This clearly indicates the potential of these molecules (and, although with exceptions, the general classes

*M*OH and *M*NC, where *M* is an alkaline earth metal Be-Ra) for direct cooling with lasers.

Nonlinear polyatomic molecules.--Examples of nonlinear polyatomic molecules having a valence electron on nonbonding orbitals are CaCH<sub>3</sub> and MgCH<sub>3</sub>. The scheme of arriving at these molecules is analogous to the one in the previous paragraph, with the obvious difference in the replacement of the pseudohalogen by methyl. The calculation results are summarized in Table II of Ref. [21]. Both molecules have quasidiagonal FC matrices for transitions between the electronic ground and first excited state (see Table II in Ref. [21]). 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 Ref. [36] for MgCH<sub>3</sub>), which also favors a quasidiagonal 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 the first stage followed by MCSCF and CI calculations, see the Supplemental Material [21]). As detailed and high-precision electronic structure calculations are beyond the scope of the current Letter, we used a simplified scheme by considering only the totally symmetric modes ( $C_{3v}$  molecular symmetry group) in estimation of FC factors rather than solving the full vibronic coupling problem. To check the influence of the nontotally symmetric modes, calculations for MgCH<sub>3</sub> were performed without symmetry restrictions and then FC factors were calculated in the harmonic approximation. Although the calculated molecular parameters are in reasonable agreement with experimental measurements (see Table II in the Supplementary Material [21]), the displacements of bond lengths M-C (M = Ca, Mg) predicted from our calculations are larger in absolute value than the experimentally measured ones (see Tables VII-X in Ref. [21]). Nevertheless, we obtained a sum of FC factors for three vibronic transitions with the largest FC factors exceeding 0.8 for MgCH<sub>3</sub>, even when nontotally symmetric modes are accounted for. Thus, one can hope for even larger values of FC factors in experiment. It should be emphasized that we primarily consider the sum of the three largest FC factors, because the value is (according to our observation) more stable to variations in relative displacements than individual FC factors. In cases where only totally symmetric modes are accounted for, the symmetry blocks are not perfectly separated due to some residual symmetry breaking in the excited state structures. Nevertheless, we obtained a sum of the three largest FC factors exceeding 0.9 for both MgCH<sub>3</sub> and CaCH<sub>3</sub>. A detailed computational investigation of Jahn-Teller vibronic coupling in these systems shall be left for future studies. We note in passing that the quite large electric dipole moment computed for CaCH<sub>3</sub> indicates the potential for Stark deceleration. Doppler temperatures for MgCH<sub>3</sub> and CaCH<sub>3</sub> can be estimated analogously to linear molecules, using calculated lifetimes of the excited states from Table III in Ref. [21]. Our order-of-magnitude estimate of  $T_D$  is the same as for linear molecules, about 1 mK.

Chiral molecules.-Cooling and trapping of chiral molecules would mean a crucial improvement for spectroscopic measurements of a number of highly interesting effects, e.g., parity violating energy differences between enantiomers due to the fundamental weak interaction [37,38]. Using the scheme from above it is also possible to identify chiral molecular structures having a quasidiagonal FC matrix. One way is isotopic substitution to a known molecule [37,39]. The chiral methyl group CHDT is well established in chemistry (see review [40] for general aspects, as well as Ref. [41] on parity violation in CHDTOH). We calculated FC factors for the molecule MgCHDT, using the same method for electronic structure calculation as in the case of MgCH<sub>3</sub>, without accounting for molecular symmetry. The resulting FC factors we obtained are as follows: (0.64, 0.18, 0.04) with  $\sum$  equal to 0.86. Thus, FC factors are predicted to be only slightly smaller than for MgCH<sub>3</sub>. This modest change 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 indicate high potential for laser cooling of such molecules to even open up the third spatial dimension for ultracold molecules generated by direct Doppler cooling with lasers.

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