Steric proficiency of polar $^2\Sigma$ molecules in congruent electric and magnetic fields

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We examine the eigenenergies, spatial orientation, and alignment of polar $^2\Sigma$ molecules subject to congruent static electric and magnetic fields. In the presence of a magnetic field only, certain pairs of Zeeman states with opposite parity intersect. Introducing a congruent electric field connects such states, thereby creating avoided crossings and a first-order Stark effect which can strongly orient the states. Since this effect, termed “steric proficiency,” operates over a narrow range of magnetic field strength, with amplitude determined by the electric dipole interaction, it should find use both for state selection and as a diagnostic tool for assigning spectral transitions. Other aspects are illustrated by strategies suggested for some prospective applications. These include a way to test whether formation of the A $^2\Sigma^+$ excited electronic state of NaO in the Na + O$_3$ reaction results from the orientation dependence of electron transfer, and techniques to enable the ground $^2\Sigma^+$ states of RbO and CsO, produced by reacting NO$_3$ with alkali atoms, to be loaded into a magnetic trap.

1 Introduction

Interactions with external electric or magnetic fields provide the chief means to manipulate rotational and translational trajectories of neutral gas-phase molecules. Recent developments include ways to orient or align the figure axis of many polar or paramagnetic molecules,1,2 and techniques to spatially trap and cool molecules to subkelvin temperatures.3 In this paper, we evaluate properties pertinent to both molecular orientation and trapping for polar $^2\Sigma$ molecules. For this simplest class of paramagnetic molecules, the eigenproperties in the presence of congruent (i.e., parallel or antiparallel) electric and magnetic fields are readily computed in terms of three dimensionless variables, enabling generic features to be mapped out for a wide range of field strengths, and molecular parameters.

For polar molecules in low rotational states, a strong electric field produces oriented pendular states, coherent superpositions or hybrids of the field-free states, in which the molecular dipole librates over a limited angular range about the field direction.4–6 This provides a simple means to spatially orient any polar molecule, since an electric dipole moment always has a fixed, anisotropic relation to body-fixed axes. For paramagnetic molecules, a strong magnetic field produces analogous pendular states, but the consequences differ.7–9 If the electronic magnetic moment is coupled to the internuclear axis, as in Hund’s cases (a) and (c), it has equiprobable projections on that axis in either direction. Accordingly, in such a magnetic pendular state, the molecular axis is aligned with respect to the field rather than oriented. (As usual, here axial anisotropy is designated orientation if it behaves like a double-headed arrow.) However, for $^2\Sigma$ molecules, or more generally any Hund’s case (b) state, the magnetic moment is only weakly coupled to the internuclear axis, but the spatial distribution of the axis can in some circumstances still exhibit a field-dependent alignment.

When a polar $^2\Sigma$ molecule is subjected to both electric and magnetic fields, a synergistic effect occurs. Particularly if the electric interaction is weak, this effect can produce much stronger orientation than attainable by the electric field alone. This arises because various pairs of Zeeman states with opposite parity become degenerate at certain values of the magnetic field. Introducing even a weak electric field connects such states, producing a first-order Stark effect which can markedly sharpen orientation of the molecule. We refer to this synergistic process, which exploits connectable degeneracies to “turn-on” a first-order interaction by combined action of fields, as steric proficiency. Elsewhere, we have treated another version, in which an intense nonresonant laser field induces nearly degenerate tunneling doublets that can be connected by a weak static electric field to produce a pseudo-first-order Stark effect.10 The resulting orientation persists only for the duration of the laser illumination, usually just a few nanoseconds. A great advantage of the steric proficiency process treated here is that no such time constraint enters, since the fields required can both be static. In effect, the joint action of electric and magnetic fields enables us to make any molecule that is polar and paramagnetic, whether linear or asymmetric, act like a symmetric top. The first-order Stark effect thereby created offers means to enhance many methods designed to manipulate molecular orientation or translation.

There is little pertinent previous work on molecules subject to combined electric and magnetic fields. Indeed, the few such experiments have pursued an exotic quest, seeking evidence for a permanent electric dipole moment of the proton, neutron, or electron as a test of time-reversal symmetry.11 Theoretical analysis of the perturbation of rotational spectra by simultaneous Stark and Zeeman fields, either congruent or perpendicular, was presented long ago,12 but without considering features that govern prospects for orientation or trapping. We have studied these aspects for $^2\Pi$, states3 and $^2\Sigma$ states13 subject to congruent fields. The case of polar $^2\Sigma$ states that we examine here is simpler, but includes the ground electronic states of many common diatomic molecules. Among these are CN, SiN, CP, XeF; the halides and hydrides of the alkaline earths, Zn, Cd, Hg; and the oxides of Rb, Cs, B, Al, Ti, Cu, Ag, Sc. We will consider $^2\Sigma$ states of alkali metal monoxides as specimens of special interest. The Na + O$_3$ reaction has been shown14,15 to yield predominately the A $^2\Sigma^+$ excited...
The Zeeman eigenproperties of \(^2\Sigma^+\) states can readily be obtained in analytic form since (as a consequence of \(AN = 0, \pm 2\)) the Hamiltonian matrix factors into blocks no larger than \(2 \times 2\). The field-dependence of the Zeeman levels is thus at most quadratic, given by

\[ E_s(J, M; \gamma) = \frac{1}{2}(E_s + E_e) \pm \frac{1}{2} \sqrt{(E_s - E_e)^2 + 4AE\gamma^2} \]

(6)

where \(E_s\) denotes the field-free levels of eqn. (2); \(AE = E_s - E_e = \gamma(N + \frac{1}{2}), x = M/(N + \frac{1}{2}),\) and \(X = B\omega_m/\Delta E\). The field-dependence becomes simply linear for the \(E_s\) or \(F_s\) states, with \(J = N + \frac{1}{2}\), when the projection has either of its extreme values, \(M = \pm J\); then eqn. (6) reduces to

\[ E_s(N + 1 \pm 1/2; X) = E_s \pm B\omega_m/2 \]

(7)

The field-dependence for all the other states, \(F_s\) or \(F_a\), also becomes linear in the high field limit (\(X \gg 1\)), where the Paschen–Back uncoupling of electron spin from molecular rotation occurs. Thus, for \(\omega_m \gg \Delta E/B\) all the Zeeman level shifts are accurately given by \(M_s\delta S_\mu_B \mu_r = \pm B\omega_m/2\); for low rotational states, this typically holds for \(\omega_m \gg 1\).

Stark states

A static electric field \(\varepsilon\) along the space-fixed \(Z\) axis subjects a linear polar molecule to an electric dipole potential,

\[ V_{el} = -\mu_z^2 \varepsilon = -\mu_z^2 \varepsilon \cos \theta = -\alpha_{el} \cos \theta \]

(8)

where the dipole moment component along the field direction \(Z\) is related to the body-fixed moment \(\mu_z^2\) along the internuclear axis \(z\) by the polar angle \(\theta\) between the \(Z\) and \(z\) axes and \(\alpha_{el} \equiv \mu_z^2/\varepsilon\) is a dimensionless interaction parameter. Since \(\alpha_{el}\) couples Hund’s case (b) states that differ in \(N\) by 0 or \(\pm 1\), the parity of the eigenstates becomes indefinite (i.e., mixed) in the presence of an electric field. Except for small \(\alpha_{el}\), where perturbation theory is adequate, analytic results are not feasible.

Consgent fields

For parallel or antiparallel static magnetic and electric fields, the Hamiltonian is

\[ H/B = H_0/B + S_Z \omega_m - \alpha_{el} \cos \theta \]

(9)

when rendered in dimensionless form by expressing energies in units of the rotational constant. The eigenproperties of this reduced Hamiltonian can be conveniently obtained from its matrix representation in a Hund’s case (a) basis, i.e., with the eigenfunctions written as

\[ \Psi = \sum_{J, M} b(J, M) |S, \Sigma, \pi, \Omega, J, M\rangle \]

(10)

where the expansion coefficients \(b(J, M)\) depend, for a given vibronic state, solely on the dimensionless interaction parameters \(\omega_m, \alpha_{el}\), and \(\gamma \equiv \mu_r/\mu_s\). The requisite matrix elements of \(H_0, S_Z, \cos \theta\) are given in the Appendix.

The range of \(J_s\) that significantly contribute to the coherent superposition of eqn. (10) increases with the interaction parameters, rendering the Hamiltonian [eqn. (9)] block-diagonal in \(M\). The projection \(\Omega\) is not a good quantum number for a \(^2\Sigma^+\) molecule, but in the field-free case \(N = J \pm \frac{1}{2}\) is. Although neither \(J\) nor \(N\) are good quantum numbers in the congruent fields, they can be employed as adiabatic labels of the states: we use \(J\) and \(N\) to denote the angular momentum quantum numbers of the field-free state that adiabatically correlates with the given state in the field(s). Since we consider a single vibronic state, we abbreviate the wavefunction as \(|N, J, M; \omega_m, \alpha_{el}, \gamma\rangle\) and label the states by \(N, J, M\).
The accuracy of the calculations is determined by the dimension of the matrix that approximates the infinite Hamiltonian. The dimension of the matrix for each $M$-block is $2(J_{\text{max}} + 1)$ with $J$ ranging between 0 and $J_{\text{max}}$. For the states and field strengths considered here, a $20 \times 20$ matrix yields an improvement of less than 1% in $E/B$ over a $10 \times 10$ matrix. We also checked the results for the purely magnetic case against the analytic solution for that case and found agreement to 6 digits. The spatial anisotropy of the molecular axis distribution is characterized by the expectation values of $\langle \cos \theta \rangle$ and $\langle \cos^2 \theta \rangle$, which specify the extent of orientation and alignment, respectively.

### 3 Results and discussion

We consider in turn the energy levels and spatial anisotropy for Zeeman, Stark and congruent fields, for states with $N \leq 2$. In figures, we use a large value for the spin–rotation parameter $\gamma = \gamma/B$ (corresponding to the $Å^2 \Sigma^+$ state of NaO, cf. Table 1), in order to exhibit the splittings between the $E_g$ pairs of states ($F_j$, $F_j$). Since prospects for magnetic trapping depend on the lowest lying state that is "low-field seeking" (i.e., the energy increases with the field strength), which is $(N, J, M) = (0, \frac{1}{2}, \frac{1}{2})$, that state is highlighted in figures showing the energy levels. Also, because the range $N \leq 2$ includes 18 distinct quantum states, to reduce congestion in the figures we use solid, dashed, and dotted curves to distinguish three categories of 6 states each, respectively designated A, B, C. As specified in Table 2, category A consists of the $F_1$ states with $M = \pm J$; category B the other $F_1$ states, and category C the $F_2$ states.

#### Zeeman field only

Fig. 1 displays the Zeeman energies from eqn. (6) as functions of the $\omega_m$ parameter, linear for $A$ states, quadratic for $B$ and $C$ states. Since both $M$ and the parity are good quantum numbers, many of the Zeeman levels cross without interacting. Of particular interest are crossings of states with the same $M$ but opposite parity (marked by circles), as these pairs of states can be coupled by a congruent Stark field. The value of the interaction parameter for such crossing points, denoted by $\omega_m^*$, can be evaluated analytically from eqn. (6) in terms of $\gamma$. Table 1 gives the resulting expressions and numerical values pertaining to the NaO($Å^2 \Sigma^+$) molecule. A special feature of $Å^2 \Sigma$ states is that, for a purely magnetic interaction, no avoided crossings of levels can occur. This is because such avoided intersections require that the levels involved have both the same parity and the same $M$, but for $Å^2 \Sigma$ molecules the Paschen–Back effect does not allow states with the same parity to intersect. This contrasts with the case of $\Sigma$ molecules where purely magnetic avoided crossings are common.

Zeeman states do not exhibit orientation but some have substantial alignment. Fig. 2 shows results for $\langle \cos^2 \theta \rangle$, which varies markedly with $\omega_m$ for the $B$ and $C$ states but not at all for the $A$ states. However, the alignment becomes independent of the field for all states in the Paschen–Back limit.

#### Stark field only

Fig. 3 shows the Stark energies as functions of $\omega_m$. At low $\omega_m$, levels with $|M|/[J(J + 1)]^{1/2} < 3^{-1/2}$ are low-field seeking. As seen in Fig. 4, for such states the space fixed dipole moment components, proportional to $\langle \cos \theta \rangle$, point the "wrong-way," i.e. antiparallel to the orienting electric field ($\langle \cos \theta \rangle < 0$). At

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**Table 1** Values of the magnetic interaction parameter $\omega_m^*$ at which levels of same $M$ but different parity intersect in $Å^2 \Sigma$ molecules

| $F_1$ | $F_2$ | Formula for $\omega_m^*$ | $\langle F_1 | \cos \theta | F_2 \rangle$ |
|-------|-------|--------------------------|----------------------------------|
| 0, $\frac{1}{2}$ | 1, $\frac{3}{2}$ | $2 - \gamma^2/2 - (\gamma^2/2)^2$ | 1.748, 0.084 |
| 1, $\frac{1}{2}$ | 2, $\frac{3}{2}$ | $4 - 3 \gamma^2/2 - (\gamma^2/2)^2$ | 3.330, 0.187 |
| 1, $\frac{1}{2}$ | 2, $\frac{3}{2}$ | $- \gamma^2 + (16 - 4\gamma^2 + (\gamma^2/2)^2)^{1/2}$ | 3.703, 0.173 |
| 1, $\frac{1}{2}$ | 2, $\frac{3}{2}$ | $\gamma^2 + (16 + 4\gamma^2 + (\gamma^2/2)^2)^{1/2}$ | 4.121, 0.358 |

*Pairs of intersecting states labeled with $N, J, M; \gamma = \gamma/B$, see text. Also given is a coupling matrix element, $\langle F_1 | \cos \theta | F_2 \rangle$. For NaO($Å^2 \Sigma$), $\gamma = 0.193$ cm$^{-1}$ and $B = 0.462$ cm$^{-1}$.16

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**Table 2** Classification of $N \leq 2$ states

<table>
<thead>
<tr>
<th>Category</th>
<th>$F$</th>
<th>$N$</th>
<th>$J$</th>
<th>$M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (solid line)</td>
<td>$F_1$</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>$F_1$</td>
<td>1</td>
<td>$\frac{1}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>$F_1$</td>
<td>2</td>
<td>$\frac{3}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
<tr>
<td>B (dashed line)</td>
<td>$F_2$</td>
<td>1</td>
<td>$\frac{1}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>$F_2$</td>
<td>2</td>
<td>$\frac{3}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
<tr>
<td>C (dotted line)</td>
<td>$F_2$</td>
<td>1</td>
<td>$\frac{1}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>$F_2$</td>
<td>2</td>
<td>$\frac{3}{2}$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
</tbody>
</table>
sufficiently high $\omega_d$, all states become “high-field seeking” (energies declining with increasing field strength), with their dipole moments oriented parallel to the field ($\langle \cos \theta \rangle > 0$). This results from angular confinement of the dipole by the $V_{st}$ potential. As $\omega_d$ increases, the Stark energy levels are drawn down into $V_{st}$, converting pinwheeling into pendular motion of decreasing amplitude. In the corresponding wavefunctions [eqn. (10)], the hybridization of $J$ states becomes increasingly extensive, thereby shrinking the pendular amplitude and increasing $\langle \cos \theta \rangle$. The $A$ states are again special, as they are high-field seeking at all field strengths and consequently for any given $N$ these states yield the strongest orientation. In Fig. 5, kindred trends with $\omega_d$ are seen in $\langle \cos^2 \theta \rangle$ in comparing the alignment with that for the field-free states. Only for the $A$ states does the alignment increase monotonically with $\omega_d$; the others all exhibit in varying extent what could be termed “wrong-way” alignment (lower than field-free) and for some states this persists even as $\omega_d$ becomes rather large.

**Congruent Zeeman and Stark fields**

Figs. 6–8 show the energy levels, orientation, and alignment for congruent fields as functions of $\omega_m$ for fixed $\omega_d = 1$. For this or weaker Stark fields, as seen in Fig. 6, the Zeeman levels are perturbed only modestly except near the crossing points at $\omega_m^*$ which now become avoided intersections. The orientation, shown in Fig. 7, now becomes sizable, however. For Zeeman fields near the $\omega_m^*$ values for pairs of intersecting states, $\langle \cos \theta \rangle$ changes abruptly, in opposite directions for members of each pair; thus low-field seeking levels switch to high-field seeking and vice-versa. The alignment, shown in Fig. 8, likewise changes abruptly near $\omega_m^*$ for each pair of intersection states. Unlike the avoided intersections seen in the energy levels, the $\langle \cos^2 \theta \rangle$ cross smoothly, and thus mark the values of $\omega_m^*$.

Figs. 9–11 show analogous results as functions of $\omega_m$, now for fixed $\omega_d = 10$, illustrating the major impact adding a strong Stark interaction has on the overall energy level structure as well as the directional properties. As seen in Fig. 9, the avoided intersections have broadened greatly and shifted to values of $\omega_m$ far removed from $\omega_m^*$. This happens because the strong Stark field mixes higher $J$ states into the hybridized pendular wavefunction [eqn. (10)]. In Figs. 10 and 11, the same broadening of the avoided intersections is evident in the directional properties. Comparison of Fig. 10 with Fig. 4, for $\omega_d = 10$ with $\omega_m = 0$, reveals the extent to which the mag-
Fig. 6  Eigenenergies (in units of the rotational constant $B$) of the states of the NaO($A^{3}\Sigma^+$) molecule in congruent electric and magnetic fields as a function of the magnetic field strength parameter $\omega_m$ at a constant electric interaction parameter $\omega_{el} = 1$. States labeled with $N, J$ and $M$. The 0, $\frac{1}{2}, \frac{3}{2}$ state (lowest low-field seeking state in the purely magnetic case) is shown by a thick line.

Fig. 7  Expectation values of the orientation cosine for the states of Fig. 6 in congruent electric and magnetic fields as a function of the magnetic field strength parameter $\omega_m$ at an electric interaction parameter $\omega_{el} = 1$. States labeled with $N, J, M$.

Fig. 8  Expectation values of the alignment cosine for the states of Fig. 6 in congruent electric and magnetic fields as a function of the magnetic field strength parameter $\omega_m$ at an electric interaction parameter $\omega_{el} = 1$. States labeled with $N, J, M$.

Fig. 9  Eigenenergies (in units of the rotational constant $B$) of the states of the NaO($A^{3}\Sigma^+$) molecule in congruent electric and magnetic fields as a function of the magnetic field strength parameter $\omega_m$ at a constant electric interaction parameter $\omega_{el} = 10$. States labeled with $N, J$ and $M$. The 0, $\frac{1}{2}, \frac{3}{2}$ state (lowest low-field seeking state in the purely magnetic case) is shown by a thick line.

Fig. 10  Expectation values of the orientation cosine for the states of Fig. 9 in congruent electric and magnetic fields as a function of the magnetic field strength parameter $\omega_m$ at an electric interaction parameter $\omega_{el} = 10$. States labeled with $N, J, M$.

Netic field influences the orientation beyond merely removing the $\pm M$ degeneracy. For each of the three $A$ states, $\langle \cos \theta \rangle$ for one of the $M$ components is unaffected by the magnetic field, whereas at sufficiently large $\omega_m$ the other $M$ component is affected because it becomes involved in an avoided intersection (cf. Fig. 1). For some of the $B$ and $C$ states, however, $\langle \cos \theta \rangle$ varies substantially at lower $\omega_m$; the magnetic field then appreciably augments or reduces the orientation that would be produced by the electric field alone. Comparison of Fig. 11 with Fig. 5 brings out similar aspects.

Two-state model for weak Stark and strong Zeeman fields

When $\omega_{el}$ is small but $\omega_m$ may be sizable, the interaction of a pair of $F_1, F_2$ states with opposite-parity and the same $M$ that cross in the purely magnetic case can be evaluated from a two-state model. This employs as basis functions the intersecting Zeeman eigenstates $\Psi_1^{(0)} = |N_1, J_1, M; \omega_m, \omega_{el} = 0\rangle$ and $\Psi_2^{(0)} = |N_2, J_2, M; \omega_m, \omega_{el} = 0\rangle$ with $F_1 = -F_2$. The corresponding energies, $E_1^{(0)}$ and $E_2^{(0)}$, may be readily obtained from eqns. (6) or (7), and from eqn. (9) the coupling matrix element
The expectation value of the orientation cosine is then

$$\langle \cos \theta \rangle = \frac{1}{2} \arctan \left( \frac{2H_{12}}{E_{1}^{(0)} - E_{2}^{(0)}} \right)$$  \hspace{1cm} (14)$$

and

$$E_{1} = \frac{1}{2} E_{1}^{(0)} (1 + \sec 2\chi), \quad E_{2} = \frac{1}{2} E_{2}^{(0)} (1 - \sec 2\chi)$$  \hspace{1cm} (13)$$

in terms of the mixing angle

$$\chi = \frac{1}{2} \arctan \left( \frac{2H_{12}}{E_{1}^{(0)} - E_{2}^{(0)}} \right)$$

The expectation value of the orientation cosine is then

$$\langle \cos \theta \rangle = \frac{1}{2} \arctan \left( \frac{2H_{12}}{E_{1}^{(0)} - E_{2}^{(0)}} \right)$$

(15)

equal in magnitude but opposite in sign for the two eigenstates. At the crossing point \(\omega_{m} = \omega_{m}^{*}\), where \(E_{1}^{(0)} = E_{2}^{(0)}\) and \(\chi = 45^\circ\) the energy exhibits a first-order Stark effect,

$$E_{1,2} = E_{1}^{(0)} \pm B \omega_{el} \langle \cos \theta \rangle^{*}$$  \hspace{1cm} (16)$$

and the orientation reaches its maximum,

$$\langle \cos \theta \rangle^{*} = \frac{1}{2} \arctan \left( \frac{2H_{12}}{E_{1}^{(0)} - E_{2}^{(0)}} \right)$$

(17)

This maximum is determined just by the unperturbed Zeeman states of eqn. (6), independent of \(\omega_{el}\). Comparison with full calculations using eqn. (10) indicates this simple two-state model is quite adequate for \(\omega_{el} = 0.001/10\).

Fig. 12 displays the variation of \(\langle \cos \theta \rangle\) with \(\omega_{m}\) and \(\omega_{el}\) as given by eqns. (14) and (15). The model shows how, in concert with a magnetic field strong enough to reach \(\omega_{m}\), a feeble electric field can produce orientation far larger than it would alone, up to a maximum \(\langle \cos \theta \rangle^{*}\) that has a fixed value for a given pair of crossing states. The range in magnetic field about \(\omega_{m}^{*}\), in which the orientation nears this maximum narrows as \(\omega_{el}\) decreases; its full width at half maximum is roughly \(\Delta \omega_{m}^{*} \approx \omega_{el}\). Accordingly, in any experiment sensitive to orientation, applying a feeble electric field and scanning the magnetic field offers a state-dependent means to switch the orientation on and off. The maximum orientation attainable by exploiting crossing states in this way, \(\langle \cos \theta \rangle^{*}\), typically will be much weaker than can be reached using a strong electric field to hybridize rotational states (cf. \(\langle \cos \theta \rangle^{*}\) in Table 1 with Fig. 4). However, in experiments often it is desirable or necessary to manage with a small \(\omega_{el}\), e.g. if the molecule has a small electric dipole moment or a large rotational constant or if the feasible electric field strength is limited by sparking or the need to reverse the field rapidly.

Figs. 13 and 14 show results obtained from eqn. (10), without recourse to the two-state model, for the energies and directionality properties of the lowest lying pair of crossing states.

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**Fig. 11** Expectation values of the alignment cosine for the states of Fig. 9 in congruent electric and magnetic fields as a function of the magnetic field strength parameter \(\omega_{m}\) at an electric interaction parameter \(\omega_{el} = 10\). States labeled with \(J, T, M\).

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**Fig. 12** Variation of the expectation value of the orientation cosine with the magnetic interaction parameter as given by eqns. (14) and (15) of the two-state model for \(\omega_{el} = 0.001, 0.005\), and 0.1. The value of \(\langle \cos \theta \rangle\) is normalized to its maximum value \(\langle \cos \theta \rangle^{*}\) which occurs at \(\omega_{m} = \omega_{m}^{*}\). See text.

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**Fig. 13** Eigenenergies and orientation and alignment cosines for the \(J, T, M = 0, 1, 1\) state (full curves) and 1, 1, 1 state (dotted curves) as a function of the magnetic field strength parameter \(\omega_{m}\) at indicated values of the electric interaction parameter \(\omega_{el}\).
states, \( F_{1}(0, \frac{1}{2}, \frac{1}{2}) \) and \( F_{2}(1, \frac{1}{2}, \frac{1}{2}) \), for NaO(A\(^2\Sigma^+\)). As seen in Table 1, in a magnetic field alone these states intersect at \( \alpha_{\text{m}} = 1.75 \). For \( \alpha_{\text{et}} = 0.1 \) and 0.2, Fig. 13 exhibits the expected quasi-resonant variation of orientation and alignment for \( \alpha_{\text{m}} \) near \( \alpha_{\text{et}} \), with both \( \langle \cos \theta \rangle \) and \( \langle \cos^2 \theta \rangle \) for the two states changing in opposite directions. Similarly, Fig. 14 shows distinct and opposite changes in the dependence on \( \alpha_{\text{et}} \) as \( \alpha_{\text{m}} \) is scanned through \( \alpha_{\text{et}} \). These features, in accord with the two-state model, blur out for larger values of \( \alpha_{\text{et}} \), as a consequence of the increasing hybridization of the rotational states.

We note that the first-order Stark effect can be induced by congruent electric and magnetic fields in any polar molecule which has definite parity in the purely magnetic case. Paramagnetic molecular states which maintain definite parity in a magnetic field include \( \Sigma^+ \) states\(^3\) or any other \( \Sigma \)-states with a higher electronic spin. Molecules in pure Hund’s case (a) or (c) states undergo mixing of their rotational states in a magnetic field and thus lose their definite parity.\(^7\)

### 4 Applications

Table 3 lists rotational constants, spin–rotation parameters, and electric dipole moments for typical ground state \( \Sigma^+ \) molecules. Most of the data are from experimental measurements or high quality theoretical calculations.\(^22^-27\). In the case of RbO and CsO, the spin–rotation constants were obtained from dipole tensor elements\(^18\) using an approximate relation,\(^36\) \( \gamma = 2(B - g_{\text{J}} - g_{\text{L}}) \), and the dipole moments are roughly approximated by values for alkali fluorides.\(^3\) Also given are values of the dimensionless interaction parameters \( \alpha_{\text{et}} \) and \( \omega_{\text{m}} \) for electric and magnetic field strengths of 100 kV cm\(^{-1}\) and 1 T, respectively. Substantially higher fields can often be used. Thus, \( \alpha_{\text{et}} \) is usually large enough to obtain quite good orientation, except for the hydride molecules and CN. Likewise, \( \omega_{\text{m}} \) is usually large enough to reach or appreciably exceed \( \omega_{\text{m}} \) for the lowest lying crossing states, with the same exceptions. Since all \( \Sigma \) molecules have a magnetic moment of one Bohr magneton, the interaction energy \( B_{\omega_{\text{m}}} / \mu_{\text{B}} = 1.3 \) K at 1 T, adequate for magnetic trapping.\(^3\)

#### NaO from Na + O\(_3\) reaction

Magnetic deflection\(^14\) and photoelectron spectroscopy\(^16\) experiments have shown that reaction of Na with \( \text{O}_3 \) gives a large yield of the low lying excited A\(^2\Sigma^+\) state of NaO but much less if any of the ground X\(^2\Pi\) state, even though the latter is energetically favored. The predominant formation of the \( \Sigma^+ \) state also seems odd in terms of qualitative chemical bonding.\(^8\) The bonding in alkali monoxides is quite ionic.\(^39\) For the \( \Pi \) state, the hole in the O\(^-\) valence shell is in a p\(_z\) oxygen orbital transverse to the internuclear axis, so two electrons reside in the p\(_z\) orbital aimed at the alkali cation. For the \( \Sigma \) state, however, the O\(^-\) hole is instead in the p\(_z\) orbital, so only one electron is directed at the cation.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( B / \text{cm}^{-1} )</th>
<th>( \gamma / \text{cm}^{-1} )</th>
<th>( \mu_{\text{el}} / \text{D} )</th>
<th>( \omega_{\text{et}} ) at 100 kV cm(^{-1})</th>
<th>( \omega_{\text{m}} ) at 1 T</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH</td>
<td>5.83</td>
<td>0.020</td>
<td>1.27(^9)</td>
<td>0.37</td>
<td>0.16</td>
</tr>
<tr>
<td>CaH</td>
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<td>0.045</td>
<td>1.14(^9)</td>
<td>0.45</td>
<td>0.22</td>
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<td>BaH</td>
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<td>0.186</td>
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<td>0.28</td>
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<td>HgH</td>
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<td>3.298(^f)</td>
<td>1.1(^*)</td>
<td>0.31</td>
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<td>MgF</td>
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<td>0.0017(^f)</td>
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<td>CaF</td>
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<td>BaF</td>
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<td>0.0027(^b)</td>
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<td>YbF</td>
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<td>0.00045(^b)</td>
<td>3.91(^*)</td>
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<td>4.45</td>
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<tr>
<td>HgF</td>
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<td>0.0159(^f)</td>
<td>4.15(^\circ)</td>
<td>7.57</td>
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<td>CaCl</td>
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<td>0.0014</td>
<td>4.47(^\circ)</td>
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<tr>
<td>BaCl</td>
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<td>0.0016(^b)</td>
<td>5.14(^\circ)</td>
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<td>CsBr</td>
<td>0.094(^w)</td>
<td>0.0033(^w)</td>
<td>4.80(^w)</td>
<td>85.78</td>
<td>9.94</td>
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<tr>
<td>CN</td>
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<td>0.0073</td>
<td>1.45</td>
<td>1.22</td>
<td>0.47</td>
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<tr>
<td>RbO</td>
<td>0.24(^*)</td>
<td>0.0199(^*)</td>
<td>(8.5)(^*)</td>
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<td>3.9</td>
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<tr>
<td>CsO</td>
<td>0.20(^*)</td>
<td>0.0076(^*)</td>
<td>(7.8)(^*)</td>
<td>65</td>
<td>4.7</td>
</tr>
</tbody>
</table>

* Unless indicated otherwise, constants taken from ref. 22.\(^\text{Ref. 22}\) Ref. 23.\(^\text{Ref. 23}\) Ref. 24.\(^\text{Ref. 24}\) Ref. 25.\(^\text{Ref. 25}\) Ref. 26.\(^\text{Ref. 26}\) Ref. 27.\(^\text{Ref. 27}\) Ref. 28.\(^\text{Ref. 28}\) Ref. 29.\(^\text{Ref. 29}\) Ref. 30.\(^\text{Ref. 30}\) Ref. 31.\(^\text{Ref. 31}\) Ref. 32.\(^\text{Ref. 32}\) Ref. 33.\(^\text{Ref. 33}\) Ref. 34.\(^\text{Ref. 34}\) Ref. 35.\(^\text{Ref. 35}\) Ref. 36.\(^\text{Ref. 36}\) Ref. 37.\(^\text{Ref. 37}\)

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This curious finding, and a kindred case\textsuperscript{40} of electronic state specificity in reactions of alkaline earth metal atoms with ClO\textsubscript{2}, has raised the question whether such specificity might be attributed to the orientation dependence of electron transfer from the metal atom to the planar reactant molecule.\textsuperscript{14,39} If an S atom (such as Na or Ca) attacks a molecule along any symmetry element, electron transfer to form an S cation cannot occur unless the parent molecule and its anion have the same symmetry. Electron transfer in a coplanar attack thus is forbidden for O\textsubscript{3} (A\textsubscript{1} parent, B\textsubscript{1} anion, so A’ \rightarrow A”) or for ClO\textsubscript{2} (B\textsubscript{1}, parent, A\textsubscript{1}, anion, so A’ \rightarrow A”) the transfer can only occur in an out-of-plane attack. For O\textsubscript{3} and ClO\textsubscript{2} the molecular orbital that receives the transferred electron is the 2b\textsubscript{1} orbital, perpendicular to the plane of the molecule. The electron transfer hence will occur most readily when the atom attacks perpendicular to the plane, which fosters reaction with the 2b\textsubscript{1} orbital of the anion aimed toward the incoming cation. If the population of this orbital goes into the \textit{p} orbital of O\textsubscript{3} the product M + O\textsuperscript{+} is formed, the \textit{p} orbital must be singly occupied (A’\Sigma\textsuperscript{+} state) in the O\textsubscript{3} reaction, and doubly occupied (A’\Sigma\textsuperscript{+} state) in the ClO\textsubscript{2} reaction. This offers an appealing but untested interpretation of the observed electronic state specificity in both reactions.

A novel stereodynamical experiment to probe the orientation dependence of the electron transfer process in the Na + O\textsubscript{3} reaction now appears feasible. It would involve three key ingredients: (i) attaining a markedly anisotropic distribution of the plane of the O\textsubscript{3} molecule; (ii) directing a beam of Na atoms parallel and perpendicular to the O\textsubscript{3} plane; and (iii) observing the consequent yield and orientation of the product NaO with respect to the O\textsubscript{3} plane. Item (i) requires aligning the molecule with respect to two space-fixed axes. As depicted in Fig. 15, ozone is a near prolate asymmetric top, with its electric dipole moment and polarizability along the \textit{a} axis (least moment of inertia, also in-plane). A strong supersonic expansion can generate a rotationally cold beam of O\textsubscript{3}, with very few molecules having nonzero rotational momentum about the \textit{a} axis (K\textsubscript{a} \approx 0). In a strong static electric field E\textsubscript{a}, the \textit{b} axis of such molecules can be substantially oriented along the static field. Planar alignment can then be achieved by subjecting the O\textsubscript{3} also to an intense nonresonant laser field E\textsubscript{b}, perpendicular to E\textsubscript{a}, thereby aligning the \textit{a} axis along the laser field \textit{via} the anisotropic polarizability interaction.\textsuperscript{10}

For item (iii), laser induced fluorescence offers both the requisite sensitivity and the capability of determining the product spatial orientation relative to the O\textsubscript{3} plane by analysis of the fluorescence polarization. Recently, the A\Sigma\textsuperscript{+} \rightarrow X\Sigma\textsuperscript{+} electronic transition of NaO has been found in the infrared via tunable diode-laser differential absorption spectroscopy.\textsuperscript{16} Over 150 rotational transitions in the lowest few vibronic bands were observed, but as yet only 14 lines of the 0–0 band have been assigned, utilizing combination differences previously determined from the microwave spectrum of the X\Sigma\textsuperscript{+} state.\textsuperscript{41} Since for the A’\Sigma\textsuperscript{+} state values of the curve-crossing parameters \(\omega_{\alpha\beta}\) reflect the value of the reduced spin–rotation constant \(\alpha\), \textit{cf.} Table 1, measurements of spectral shifts in the presence of congruent magnetic and electric fields should facilitate assignment of many more transitions. This would enable laser-induced fluorescence spectra, produced by exciting the A’\Sigma\textsuperscript{+} state to a higher optically accessible state,\textsuperscript{38} to be employed to analyze the vibronic and rotational state distributions of NaO from the Na + O\textsubscript{3} reaction. Exploiting the steric propensity of the A’\Sigma\textsuperscript{+} state should also usefully enhance the measurements of fluorescence polarization that item (iii) requires.

**Prospects for trapping MO molecules**

Since the forces available to trap neutral atoms or molecules are weak, a prerequisite for trapping is a means to lower markedly their translational kinetic energy, typically below 1 K. Once trapping is accomplished, further cooling to microkelvin temperatures can be attained.\textsuperscript{3} For molecules the fusion of vibrational and rotational energy levels precludes optical cooling, particularly effective for alkali atoms. Several other methods are being pursued,\textsuperscript{43–50} although thus far only two have achieved a marked trapping/cooling of molecules. In a prototype experiment, CaH molecules formed by laser ablation werecollisionally relaxed by \(^3\text{He}\) buffer-gas to about 0.3 K and confined in a magnetic trap.\textsuperscript{4} The other successful approach created alkali dimer molecules, in small yield but already quite translationally cool (\(\approx 300\) \(\mu\)K), within an alkali atom trap by photoassociation\textsuperscript{48,49} or ternary recombination.\textsuperscript{50} Here we consider how RbO or CsO, generated by chemical reaction, might be loaded into a magnetic trap.

In contrast to NaO, the ground electronic state of RbO and CsO is \(X\Sigma\textsuperscript{+}\) and the first excited state is A’\Sigma\textsuperscript{+}. The reaction of M = Rb or Cs with NO\textsubscript{3} is nearly thermoneutral (within the uncertainties in the bond strengths\textsuperscript{13}), and forms MO predominantly or solely in the \(\Sigma\textsuperscript{+}\) ground state.\textsuperscript{17,18} Like most reactions of alkali atoms with highly electrophilic molecules, M + NO\textsubscript{3} appears to have no activation energy and a very large reaction cross section, \(>100\) \(\text{Å}^2\). These properties suggest delivering MO molecules into the cold buffer-gas by the gentler means of reaction rather than laser ablation; we note two variants: (i) gaseous NO\textsubscript{3} might be injected by a conventional molecular beam source into the buffer-gas and react with previously trapped and cooled alkali atoms; (ii) the MO molecules could first be deposited in a rare gas matrix,\textsuperscript{18} then liberated by laser desorption within the trap.

Since the buffer-gas cools molecules rotationally as well as translationally, a guest molecule interacts with the trapping field \textit{via} its lowest rotational state. If the molecule is to be trapped, that state must be low-field seeking, \textit{i.e.} with eigenenergy that increases with field strength, so that the molecule will experience a force towards the trap bottom, where the field strength is minimal. As seen in Fig. 1, for any \(\Sigma\textsuperscript{+}\) molecule the lowest rotational state indeed correlates with a low-field seeking (0, \(\Omega_\text{J}M=0\)) state. In contrast, as seen in Fig. 3, this very state is high-field seeking in an electrostatic field. Also, as seen in Fig. 6, even a weak electric field would usually handicap the initial loading of a magnetic trap, since it would cause the \((0, \frac{1}{2}, \frac{1}{2})\) state to become high-field seeking above the curve-crossing point, \(\omega_{\alpha\beta}\). However, the situation changes after the initial loading and removal of the buffer gas.\textsuperscript{5} Since the molecules can then be

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**Fig. 15** Principal axes of inertia, electric dipole moment and polarizability of ozone. At mutually perpendicular static electric and radiative fields of 150 \(\text{kV cm}^{-1}\) and 10\textsuperscript{15} \(\text{W cm}^{-2}\) the corresponding interaction parameters are estimated to be \(\omega_{\alpha\beta}=2.8\) (\(\mu_{\alpha}\) = 0.6 D, \(B=0.44\) cm\(^{-1}\) and \(\Delta \omega=8.7\) (polarizability anisotropy \(\Delta \lambda = 3.1\) \(\text{Å}^2\), \(A=1.55\) cm\(^{-1}\) yielding a spatial confinement of the ozone’s plane for the \(J=0, M=0\) state with an angular amplitude of about \(\pm 38^\circ\) with respect to \(b\)-axis and about \(\pm 47^\circ\) with respect to \(a\)-axis. Molecular parameters of ground-state O\textsubscript{3} taken from refs. 22 and 42.
cooled much further, a weaker magnetic field suffices to retain them in the trap. In this post-loading regime, an electric field could be introduced to orient the molecules.

**Search for EDM**

Currently, the experimental upper bound on a possible permanent electric dipole moment (EDM) of the electron is about $2 \times 10^{-18}$ D.\(^\text{1}\)\(^\dagger\) sufficient to narrow somewhat the range of theoretical contenders for particle physics beyond the standard model.\(^\text{53}\) Improving the bound by tenfold or more is in prospect, however, and would provide a much more stringent test of theoretical predictions. Ironically, the most promising approach calls for experiments using molecules.\(^\text{19}\) Within molecules containing a high-Z atom, such as BaF, YbF, or HgF, an unpaired electron is subject to a huge effective internal electric field, of the order 10 GV cm\(^{-1}\).\(^\text{52,53}\) The EDM experiment requires spatially polarizing the electron spin (along which its electric dipole, if any, must point) in an external magnetic field and also orienting the huge internal field by orienting the polar molecule with an external electric field. An elegant interferometric technique is then used to search for tiny frequency shifts associated with reversing the field directions.\(^\text{51}\)

In the EDM search it is desirable to have the largest feasible magnitude for $\langle \cos \theta \rangle$. Although sizable values can be readily attained for the low rotational levels (cf. Table 3 and Fig. 4), in the molecular beam or vapor cell techniques so far used, these levels are sparsely populated. Also, the thermal velocities of the molecules seriously limit the time available to produce observable interferometric phase shifts. Trapping and ultracooling the molecules thus could greatly enhance the EDM experiment. The molecules of interest are all good candidates for magnetic trapping and the obstacles and options are essentially those noted above for MO molecules. Perhaps the steric proficiency of molecules, induced by cooperative electric and magnetic fields, will lead to a synergistic interaction between physical chemistry and particle physics.

**Acknowledgement**

We dedicate this paper to the memory of Roger Grice. Curve-crossing processes, magnetic fields, and electronic structure interpretations akin to those treated here were among the early and abiding themes of his zesty pursuit of molecular reaction dynamics. Support of this work by the National Science Foundation is gratefully acknowledged.

**6 Appendix**

The eigenproblem was set up in a Hund’s case (a) basis,\(^\text{20}\) for which the nonvanishing matrix elements of the field-free Hamiltonian are

$$\begin{align*}
\langle S, \pm \frac{1}{2} | J, \Omega, M | H_0 | S, \pm \frac{1}{2} \rangle &= B \left( J + \frac{1}{2} \right)^2 - \frac{7}{2} \quad (18) \\
\langle S, \pm \frac{1}{2} | J, \Omega, M | H_0 | S, \pm \frac{1}{2} \rangle &= \left( \frac{7}{2} - B \right) \left( J + \frac{1}{2} \right) \quad (19)
\end{align*}$$

Since the electronic magnetic dipole moment is proportional to its spin, transforming the dipole from body-fixed to space-fixed coordinates requires only matrix elements of the spin and direction cosines; thus

$$S_x = \left[ \frac{1}{2} \Phi_z S^- + \Phi_x S^+ + \Phi_y S^z \right]$$

where the superscripts pertain to the body-fixed system, the subscripts to the space-fixed system. The electron spin matrix elements are

$$\begin{align*}
\langle S, \pm \frac{1}{2} | J, \Omega, M | S, \pm \frac{1}{2} \rangle | J, \Omega, M \rangle &= 1 \quad (21) \\
\langle S, \pm \frac{1}{2} | J, \Omega, M | S, \mp \frac{1}{2} \rangle | J, \Omega, M \rangle &= \frac{1}{2} \quad (22)
\end{align*}$$

The electric dipole interaction requires only

$$\Phi_z = \cos \theta$$

The matrix elements of the direction cosine operator $\Phi$ needed here given in ref. 21.

**References**


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