Diatomic molecules in optical and microwave dipole traps

Marius Lysebo[1] and Leif Veseth[2]
[1]*Faculty of Engineering, Oslo University College, NO-0130 Oslo, Norway*
[2]*Department of Physics, University of Oslo, NO-0316 Oslo, Norway*

(Received 22 December 2010; published 11 March 2011)

The dipole forces on rotating diatomic molecules are worked out in detail for optical as well as microwave radiation fields. The objective is in particular to investigate how the dipole forces and potentials depend on the subtle internal structure of the molecule, with special emphasis on hyperfine and Zeeman states. Dipole potentials are obtained from computations of the real part of the complex molecular polarizability, whereas the imaginary part yields the scattering force. Numerical examples are presented for ^{23}Na$_2$ and OH for optical (laser) fields related to strong electronic transitions and for microwave fields for the Λ doubling in the OH ground state.

DOI: 10.1103/PhysRevA.83.033407 PACS number(s): 37.10.Pq, 33.80.−b, 37.10.Jk

I. INTRODUCTION

The study of cold or ultracold molecules is a branch of physics that attracts much attention at present. Compared to the even more active field of ultracold atoms, molecules represent extra challenges, as well as extra opportunities. Well-established methods to cool and trap atoms will generally not work for molecules, or the standard methods will cause extra complications in the molecular case. The present work will address the problem of trapping diatomic molecules by means of optical- or generally electromagnetic dipole forces. The trapping of neutral atoms in optical dipole potentials, e.g., optical lattices, represents at present a standard method for handling ultracold atoms [1,2]. The theory behind the atomic optical dipole trapping is normally based on the assumption that the atom has a simple two-level internal structure. For diatomic molecules there are more internal degrees of freedom which lead to more complex patterns of energy levels. These extra complexities, however, open new opportunities to study a variety of dipole potentials that depend on the specific internal molecular state.

So far there seems to be few studies of the dipole forces on diatomic molecules. Kotochigova and Tiesinga [3] have made a theoretical investigation of the interaction of polar molecules with optical lattices and microwave fields. A detailed discussion of the possibility of trapping polar molecules in a microwave cavity was carried out by DeMille *et al.* [4]. However, both these studies were limited to molecular vibrational and rotational states, leaving out the interesting and characteristic effects related to hyperfine and Zeeman levels. There are at present numerous articles reporting on experiments in which cold molecules are held in optical dipole traps or lattices as part of the production or cooling process. The general trend is, however, that there is little or no discussion on details regarding the trapping forces. A recent overview of articles in the field is found in a special issue of *New Journal of Physics* [5], also with a large number of further references.

The objective of the present work is to make a theoretical analysis of the dipole force on diatomic molecules, with special emphasis on the finer internal structure details, like hyperfine and Zeeman interactions. The small hyperfine and Zeeman splittings themselves are not necessarily of great importance, as the relevant resonance frequencies will be much larger. The important effects arise from the dependencies of the dipole matrix elements on the hyperfine and Zeeman quantum numbers. This is particularly pronounced for molecules, where the interaction is between a "space fixed" external field and the subtle internal states of a rotating molecule. It will turn out that the trapping force or potential might be strongly dependent on the actual internal level of the molecule and also on the state of polarization of the external laser or microwave field. This might in turn lead to interesting opportunities for experimental handling of the molecules in dipole traps or lattices, including the potential for making workable molecular qubits [6,7].

II. INTERACTION WITH AN EXTERNAL ELECTRIC LIGHT FIELD

A. General theory

The Hamiltonian for an atomic or molecular system interacting with an external electric field $\vec{\mathcal{E}}$ takes the form

$$H' = -\vec{D}\cdot\vec{\mathcal{E}} = -\sum_{\mu=-1}^{1}(-1)^{\mu}D_{-\mu}\mathcal{E}_{\mu}, \tag{1}$$

where $\vec{D}$ denotes the electric dipole moment given by $\vec{D} = \sum_i q_i\vec{r}_i$, where the sum extends over electrons and nuclei and $\vec{\mathcal{E}}$ is the external electric field. The spherical components are defined as

$$\mathcal{E}_{\pm 1} = \mp\frac{1}{\sqrt{2}}(\mathcal{E}_x \pm i\mathcal{E}_y), \quad \mathcal{E}_0 = \mathcal{E}_z. \tag{2}$$

We now assume that the electric field has just one component μ. For a light field $\mu = 1$and $\mu = -1$ respectively means left and right circular polarization, whereas $\mu = 0$ means linear polarization. Furthermore, we will in the present work consider the light field from two counter propagating polarized light waves so that the electric field components take the form

$$\mathcal{E}_{\mu} = \mathcal{E}_{\mu}(\vec{r})[e^{i\omega t} + e^{-i\omega t}] = 2\mathcal{E}_{\mu}(\vec{r})\cos\omega t. \tag{3}$$

In this case the light-atom–molecule interaction leads to a time-averaged potential energy (light shift) given by

$$U_{\text{dip}} = -\tfrac{1}{2}\alpha_{n,-\mu}(\omega)\left\langle\mathcal{E}_{\mu}^{2}\right\rangle, \tag{4}$$

where the dynamic polarizability $\alpha_{n,-\mu}(\omega)$ for the state $|\Psi_n\rangle$ is given by the expression

$$\alpha_{n,-\mu}(\omega) = -\sum_{k\neq n} |\langle\Psi_n|D_{-\mu}|\Psi_k\rangle|^2 \times \left[\frac{1}{E_n - E_k + \hbar\omega} + \frac{1}{E_n - E_k - \hbar\omega}\right]. \quad (5)$$

$E_n$andE_k denote the energies of the respective states n and k. Finally, the intensity of the light field takes the form $I_\mu(\vec{r}) = 2\varepsilon_0 c|\mathcal{E}_\mu(\vec{r})|^2$, and the expression for the potential of Eq. (4) is recast as

$$U_{\text{dip}}(\vec{r}) = -\frac{1}{2\varepsilon_0 c}\alpha_{n,-\mu}(\omega) I_\mu(\vec{r}). \quad (6)$$

The finite life time of the excited states $|\Psi_k\rangle$ due to spontaneous emission may effectively be included through the simple replacement $E_k \rightarrow E_k - \frac{i}{2}\hbar\Gamma_k$ for the energies in the expression for the polarizability $\alpha_{n,-\mu}(\omega)$, which then reads

$$\alpha_{n,-\mu}(\omega) = -2\sum_{k\neq n}\frac{\left(E_n - E_k + \frac{i}{2}\hbar\Gamma_k\right)|\langle\Psi_n|D_{-\mu}|\Psi_k\rangle|^2}{\left(E_n - E_k + \frac{i}{2}\hbar\Gamma_k\right)^2 - \hbar^2\omega^2}. \quad (7)$$

The transition rate Γ_k for spontaneous transitions from the state $|\Psi_k\rangle$ to all other lower accessible states $|\Psi_l\rangle$ is given by [1,8,9]

$$\Gamma_k = \frac{1}{3\pi\varepsilon_0 c^3 \hbar^4}\sum_l \sum_{\nu=-1}^{1} (E_k - E_l)^3 |\langle\Psi_k|D_\nu|\Psi_l\rangle|^2. \quad (8)$$

Thus, taking into account spontaneous emission the potential finally takes the form

$$U_{\text{dip}}(\vec{r}) = -\frac{1}{2\varepsilon_0 c}\text{Re}[\alpha_{n,-\mu}(\omega)] I_\mu(\vec{r}), \quad (9)$$

and the rate Γ_{sc} of photons absorbed and reemitted (scattered) at a given frequency ω is given by [1].

$$\Gamma_{\text{sc},n}(\vec{r},\omega) = \frac{1}{\hbar\varepsilon_0 c}\text{Im}[\alpha_{n,-\mu}(\omega)] I_\mu(\vec{r}). \quad (10)$$

Generally, the imaginary part of the complex polarizability yields the strength of absorption. This connection is also extensively used to compute photoionization cross sections, e.g., Ref. [10].

B. Rotating diatomic molecules

Next we have to specify the molecular states $|\Psi_n\rangle$ and $|\Psi_k\rangle$. In the diatomic case they may be expanded in terms of molecular basis functions of the form

$$|\Psi_a\rangle = |q\nu\Lambda\Sigma SJIFM_F\rangle, \quad (11)$$

where q indicates the relevant electronic state, ν is a corresponding vibrational quantum number, Λ and Σ refer to the quantized components of the electronic orbital and spin angular momenta along the molecular axis, and J denotes the total molecular angular momentum except for nuclear spin. This rovibronic part of the basis is referred to as Hund's coupling case (a) [11]. I refers to the total nuclear spin, $\vec{F} = \vec{J} + \vec{I}$, and M_F denotes the quantized component of $\vec{F}$ along a space fixed axis.

The general basis functions given in Eq. (11) may be more conveniently represented in a decoupled way, factorizing out the nuclear spin part [12,13]:

$$|\Psi_a\rangle = \sum_{M_J,M_I} (-1)^{J-I+M_F}(2F+1)^{1/2}\begin{pmatrix} J & I & F \\ M_J & M_I & -M_F \end{pmatrix} \times |q\nu\Lambda\Sigma SJM_J\rangle|IM_I\rangle, \quad (12)$$

with $M_J + M_I = M_F$, and where M_J and M_I respectively refer to the quantized components of $\vec{J}$ and $\vec{I}$ along a space fixed axis. In a similar way the nuclear spin state $|IM_I\rangle$ may be given in a decoupled form:

$$|IM_1\rangle = \sum_{M_{I_1},M_{I_2}} (-1)^{I_1-I_2+M_I}(2F+1)^{1/2}\begin{pmatrix} I_1 & I_2 & I \\ M_{I_1} & M_{I_2} & -M_I \end{pmatrix} \times \left|I_1 I_2 M_{I_1} M_{I_2}\right\rangle. \quad (13)$$

Here $I_1, M_{I_1}, I_2,$andM_{I_2} refer to the nuclear spins of the two nuclei, I_1 and I_2 have fixed values.

To work out the matrix elements of the space fixed components of the dipole moment in Eqs. (7) and (8) we also have to take into account the molecular symmetries. For a general diatomic molecule there are two basic symmetri operators: the inversion E^* of the coordinates of all electrons and nuclei and a reflection σ_v of the electron positions in a plane containing the molecular axis. The effect of the total inversion operator E^* (parity) on a Hund's case (a) basis state is given by [14–18]:

$$E^*|q\nu\Lambda\Sigma SJM_J\rangle = (-1)^{J-S+S_n}|q\nu - \Lambda - \Sigma SJM_J\rangle, \quad (14)$$

where s_n is related to the reflection symmetry σ_v through the relation

$$\sigma_v|q\nu\Lambda\Sigma SJM_J\rangle = (-1)^{S_n}|q\nu - \Lambda - \Sigma SJM_J\rangle, \quad (15)$$

Here we have $s_n = 0$ for $\Lambda \neq 0$ and for Σ^+ molecular states, whereas $s_n = 1$ for Σ^- states. Thus, eigenstates for the inversion operator E^* are obtained by forming the linear combination

$$|\Phi_a\rangle = \frac{1}{\sqrt{2}}[|q\nu\Lambda\Sigma SJM_J\rangle] + (-1)^s|q\nu - \Lambda - \Sigma SJM_J\rangle, \quad (16)$$

with eigenvalues given by

$$E^*|\Phi_a\rangle = (-1)^{J-S+S_n+S}|\Phi_a\rangle, \quad (17)$$

For given values of $J, S,$ands_n the value of s may be chosen as 0 or 1 to give the two possible eigenvalues for E^*.

Now, the matrix elements of the dipole operator are diagonal in the nuclear spin quantum numbers IandM_I [cf. Eq. (12)] and also independent of these quantum numbers except for the 3j symbol in Eq. (12). Hence, we may concentrate on the symmetrized space and electronic spin states of Eqs. (16) and (17). Working out the matrix element we obtain

$$\langle\Phi_a|D_{-\mu}|\Phi'_a\rangle = \tfrac{1}{2}[1 - (-1)^{J+J'-2S+s_n+s'_n+s+s'}] \times \langle q\nu\Lambda\Sigma SJM_J|D_{-\mu}|q'\nu'\Lambda'\Sigma SJ'M'_J\rangle, \quad (18)$$

with $\Lambda \geqslant 0$ and $\Lambda' \geqslant 0$. For the special case $\Lambda = \Lambda' = 0$ we have to set $\Sigma \geqslant 0$. Primed quantities all refer to $|\Phi_a{}'\rangle$. However, the special cases $\Lambda > 0$ and $\Lambda' = \Sigma' = 0$, or $\Lambda = \Sigma = 0$ and $\Lambda' > 0$, have to be handled separately, and the result is

$$\langle \Phi_a | D_{-\mu} | \Phi'_a \rangle = \frac{1}{\sqrt{2}} [1 - (-1)^{J+J'-2S+s_n+s'_n+s''}] \times \langle q v \Lambda \Sigma S J M_J | D_{-\mu} | q' v' \Lambda' \Sigma S J' M_J{}' \rangle. \tag{19}$$

Here s'' equals s for $\Lambda \neq 0$ and s' for $\Lambda' \neq 0$ [cf. Eq. (16)]. By the derivation of Eqs. (18) and (19) we have used the fact that $D_{-\mu}$ changes sign under the operation E^*. Equations (18) and (19) clearly show the selection rules we have to observe to have dipole matrix elements differ from zero.

C. Homonuclear diatomic molecules

For a homonuclear diatomic molecule there are two extra symmetry operations denoted (12) and i, where i represents inversion of the electronic coordinates through the midpoint between the nuclei, and (12) interchanges the coordinates of the two nuclei. From the expression for $|I M_I\rangle$ in Eq. (13) we notice that an interchange of the two nuclei merely results in an interchange of the quantum numbers M_{I_1} and M_{I_2} in the $3j$ symbol, and with $I_1 = I_2$, this leads to a factor $(-1)^{I_1+I_2+I}$, and consequently

$$(12)|I M_I\rangle = (-1)^{I_1+I_2+I} |I M_I\rangle. \tag{20}$$

For a homonuclear molecule we have the following simple relation between the symmetry operators

$$(12) = E^* i. \tag{21}$$

Hence, Eqs. (14) and (17) yield

$$(12)|q v \Lambda \Sigma S J M_J\rangle = (-1)^{J-S+s_n+s+s_i} |q v - \Lambda - \Sigma S J M_J\rangle, \tag{22}$$

where s_i refers to the eigenvalues of the electronic inversion operator i, i.e., $s_i = 0$ for electronic g states and $s_i = 1$ for u states. For homonuclear molecules the total molecular state, including nuclear spin, has to be antisymmetric under (12) for Fermionic nuclei ($I_1 = I_2 = \text{half} - \text{integer}$), and symmetric for bosons ($I_1 = I_2 = \text{integer}$). From Eqs. (20) and (22) we then have the following allowed combinations.

From Eqs. (11), (12), and (17) we may now write down the expression for the dipole matrix element for two general symmetrized molecular states $|\Psi\rangle$ and $|\Psi'\rangle$:

$$\langle \Psi | D_{-\mu} | \Psi' \rangle = \sum_{M_J, M_I} \sum_{M_J{}'} (-1)^{J+J'-2I+M_F+M'_F} \times [(2F+1)(2F'+1)]^{1/2} \begin{pmatrix} J & I & F \\ M_J & M_I & -M_F \end{pmatrix} \times \begin{pmatrix} J' & I & F' \\ M_J{}' & M_I & -M'_F \end{pmatrix} \langle \Phi_a | D_{-\mu} | \Phi'_a \rangle \tag{23}$$

The last factor in the equation above is obtained from Eqs. (18) or (19).

What remains to be worked out is the dipole matrix element of Eqs. (18) and (19). The complication here arises from the fact that the dipole moment component $D_{-\mu}$ refers to a space-fixed coordinate system, whereas the molecular state is expressed in terms of coordinates and variables referred to a molecule-fixed system. There is, however, a rather simple relation between space-fixed and molecule-fixed components [13,16,18]:

$$\begin{aligned} &\langle q v \Lambda \Sigma S J M_J | D_{-\mu} | q' v' \Lambda' \Sigma S J' M_J{}' \rangle) \\ &= \sum_{\nu=-1}^{1} \langle q v \Lambda | d_\nu | q' v' \Lambda' \rangle (-1)^{M_J{}' - \Omega' - \nu - \mu} \\ &\quad \times [(2J+1)(2J'+1)]^{1/2} \\ &\quad \times \begin{pmatrix} J & 1 & J' \\ \Omega & -\nu & -\Omega' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ M_J & \mu & -M_J{}' \end{pmatrix}. \end{aligned} \tag{24}$$

Here $\Omega = \Lambda + \Sigma$ and $\Omega' = \Lambda' + \Sigma'$, and d_ν denotes spherical components of the dipole operator in the molecule fixed coordinate system. We notice from Eq. (24) that for given values of Ω and Ω' just one component d_ν contributes, i.e., $\nu = \Omega - \Omega' = \Lambda - \Lambda'$.

For a homonuclear molecule there is no nuclear contribution to the electric dipole moment, as the origin is placed midway between the nuclei. The inversion symmetry i leads to an additional selection rule, as it is clear from Eq. (24) that the matrix element for d_ν will be zero unless the two states have opposite eigenvalues of i (g-u selection rule).

D. Intermediate coupling

Generally, a molecular state does not take the simple form of a case(a) basis function [cf. Eqs. (11) and (12)]. In a more general intermediate coupling the case (a) basis will be replaced by linear combinations of the form

$$|q v \Lambda S J M_J\rangle = \sum_{\Sigma=-S}^{S} C_\Sigma |q v \Lambda \Sigma S J M_J\rangle. \tag{25}$$

The coefficients C_Σ are obtained by diagonalizing a Hamiltonian matrix containing several molecular parameters like the rotational constant and the spin-orbit coupling constant. A molecular state of Σ symmetry ($\Lambda = 0$) will normally be close to a Hund's case (b) state, which in terms of the case (a) basis is expressed as [16,18]

$$|q v \Lambda N S J M_J\rangle = (2N+1)^{1/2} \sum_{\Sigma=-S}^{S} (-1)^{J-\Sigma-\Lambda} \times \begin{pmatrix} N & S & J \\ -\Lambda & -\Sigma & \Omega \end{pmatrix} |q v \Lambda \Sigma S J M_J\rangle. \tag{26}$$

Here the quantum number N represents the total molecular orbital angular momentum $\vec{N} = \vec{J} - \vec{S}$, which is quantized in the case (b) basis.

E. Sum rules

Using known summation rules for the $3j$ symbols, we obtain after some algebra the following rather simple sum rules for the dipole matrix elements [cf. Eqs. (11), (13), and (14)]:

$$\sum_{M_F}\sum_{F',M_F'}|\langle q\nu\Lambda\Sigma SJIFM_F|D_{-\mu}|q'\nu'\Lambda'\Sigma SJ'IF'M_F'\rangle|^2 = \frac{1}{3}|\langle q\nu\Lambda|d_\nu|q'\nu'\Lambda'\rangle|^2(2F+1)(2J'+1) \times \begin{pmatrix} J & 1 & J' \\ \Omega & -\nu & -\Omega' \end{pmatrix}^2. \tag{27}$$

We notice that the sum is independent of the space fixed component -μ, which is also reflected by the factor 1/3 in front of the expression on the right-hand side. In the expression for the complex polarizability given by Eq. (7) the energy difference $E_n - E_k + \frac{i\hbar}{2}\Gamma_k$ will have an insignificant dependence on F', M_F', and M_F if the energies E_n and E_k refer to different electronic or vibrational energies. Thus, the sum rule of Eq. (27) may be very useful for computing polarizabilities in such cases.

Another useful sum rule might be the following:

$$\sum_{\nu=-1}^{1}\sum_{F',M_F'}|\langle q\nu\Lambda\Sigma SJIFM_F|D_\nu|q'\nu'\Lambda'\Sigma SJ'IF'M_F'\rangle|^2 = |\langle q\nu\Lambda|d_{\nu'}|q'\nu'\Lambda'\rangle|^2\,(2J'+1)\begin{pmatrix} J & 1 & J' \\ \Omega & -\nu' & -\Omega' \end{pmatrix}^2. \tag{28}$$

This sum rule may be very useful for computing transition rates according to Eq. (8), since in this case we also have to make a summation over all polarizations ν of the radiation field. Furthermore, we notice that the sum in Eq. (28) above is independent of the initial state quantum numbers F and M_F.

For the more general intermediate case of Eq. (25) analogs to the sum rules of Eqs. (27) and (28) also exist. However, the squared 3j symbols in these equations will have to be replaced by somewhat more complex double sums involving the coefficients C_Σ and $C_{\Sigma'}$, which normally will not depend on F or M_F.

III. EXAMPLES

A. The ^{23}Na$_2$ molecule in an optical field

As a first example we will consider the prospects for trapping a ^{23}Na$_2$ molecule in its electronic, vibrational, and rotational ground state. From the $X^1\Sigma_g^+$ ground state there is a strong transition to the excited $A^1\Sigma_u^+$ electronic state. The electric dipole transition element $\langle q\nu\Lambda|d_\nu|q'\nu'\Lambda'\rangle$ of Eq. (24) in this case takes the form

$$\langle X^1\Sigma_g^+, v=0|d_0|A^1\Sigma_u^+, v'\rangle, \tag{29}$$

with a maximum value of 1.67 a.u. for $v'=8$. The dipole matrix elements needed for the present investigation were calculated from potential curves and dipole transition elements versus R given by Stevens and Hessel [19]. Starting from the lowest rotational level $J=0$ with parity +1, only the rotational level $J'=1$ with parity −1 for the excited $A^1\Sigma_u^+$ state is attainable in an electric dipole transition (cf. Fig. 1). For the ^{23}Na$_2$ molecule we have $I_1 = I_2 = 3/2$, and Table I yields the following allowed combinations: $X^1\Sigma_g^+$, $J=0$: $I=2$, $F=2$, and $I=0$, $F=0$, $A^1\Sigma_u^+$, $J=1$: $I=2$, $F=3, 2, 1$, and $I=0$, $F=1$.

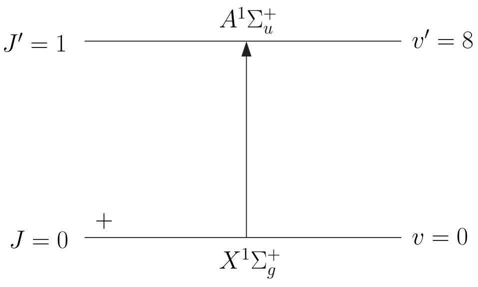

FIG. 1. The proposed trapping transition for ^{23}Na$_2$.

TABLE I. Allowed combinations of quantum numbers and symmetry labels for homonuclear diatomic molecules.

	I_1+I_2+I	$J-S+s_n+s+s_i$
Fermions	Even	Odd
	Odd	Even
Bosons	Even	Odd
	Odd	Even

The energy difference for the transition $v=0$, $J=0$ to $v'=8$, $J'=1$ is approximately 4.670×10^8 MHz (15 575 cm^{-1}), and the detuning in the subsequent calculations are with reference to this center frequency. Now, there are very significant values of the matrix element of Eq. (29) for several vibrational states around $v'=8$. In the present calculations of the polarizability $v'=6$, 7, 9, and 10 were also included in addition to the resonance level $v'=8$. The energy difference between adjacent vibrational levels around $v'=8$ is approximately 110 cm^{-1} ≈ 3300 GHz. Thus, the detuning will be kept less than half of this energy difference.

To compute the basic complex polarizability $\alpha_{n,-\mu}(\omega)$ of Eq. (7) we need the rates Γ_k for spontaneous emission from the various levels E_k included in the calculation, i.e., the rotational level $J'=1$ of the $A^1\Sigma_u^+$ vibrational levels v′ = 6–10. Here transitions from the upper state to all accessible lower states for all polarizations (μ) have to be included. The sum rule of Eq. (28) is in particular useful for this purpose, showing that the transition rate is independent of the upper state quantum numbers I, F, and M_F. Transition rates and lifetimes for a series of vibrational and rotational levels of the $A^1\Sigma_u^+$ state were calculated by Stevens and Hessel [19]. According to their results the transition rates are quite independent on the vibrational or rotational state, also in good agreement with observed lifetimes. From the results of Stevens and Hessel we have adopted the value $\Gamma_k = 1.90\times10^{-9}$ a.u. $= 7.8\times10^7$ s^{-1} for the transition rates for all the vibrational levels $v'=6$–10 of present interest.

The complex polarizability was calculated from Eq. (7), also with application of the convenient sum rule of Eq. (27). Computed real- and imaginary polarizabilities were obtained for various values of $\hbar\omega$, detuned from the $v=0\to v'=8$ transition frequency. The results obtained are given in Table II. Subsequently the depth of the dipole potential $U_{\rm dip}$ and the rate of scattered photons $\Gamma_{\rm sc}$ were obtained from Eqs. (9)

TABLE II. Computed potential depths and scattering rates for $^{23}\mathrm{Na}_2$. Similar positive (blue) detunings give quite identical numerical results, with a change of sign for for $\mathrm{Re}(\alpha)$. The intensity of the laser light is set to 10^3 W cm^{-2}.

Detuning (GHz)	$\mathrm{Re}(\alpha)$ (a.u.)	$\mathrm{Im}(\alpha)$ (a.u.)	U_{dip} (MHz)	Temperature (K)	Scattering rate $\Gamma_{\mathrm{sc}}(\mathrm{s}^{-1})$	Lifetime τ (s)
−500	2.29×10^4	0.323	1.05	1.0×10^{-4}	186	0.13
−1000	9.18×10^3	0.097	0.42	4.0×10^{-5}	56	0.18
−1500	3.11×10^3	0.064	0.14	1.3×10^{-5}	37	0.091

and (10) respectively, with an assumed intensity of the laser light of 1000 W cm^{-2}. Neglecting the small nuclear spin-spin coupling, there is no degeneracy in the $^{23}\mathrm{Na}_2$ ground state. Representing the initial state by a mixed state of the form

$$|\Psi_n\rangle = \frac{1}{\sqrt{2F+1}} \sum_{M_F=-F}^{F} |q v \Lambda \Sigma S J I F M_F\rangle, \qquad (30)$$

it is seen from Eq. (27) that neither the potential nor the scattering rate will depend on the initial state quantum numbers I, F, or M_F, and even not on the state of polarization (μ) of the laser light.

The temperatures listed in Table II were obtained according to the simple relation $\frac{1}{2}k_B T = U_{\mathrm{dip}}$. We notice from Table II that trapping of the $^{23}\mathrm{Na}_2$ molecules by the present mechanism requires that they are precooled to about 10^{-5} K. The recoil energy for emission or absorption of a photon is given by

$$E_{\mathrm{rec}} = \frac{\hbar^2\omega^2}{2Mc^2}, \qquad (31)$$

and in the present case we have $E_{\mathrm{rec}} \approx 0.021$ MHz. Assuming an energy transfer of two times E_{rec} pr. scattering, the lifetime τ of the molecule in the trap may be estimated from the relation

$$2\tau\Gamma_{\mathrm{sc}}E_{\mathrm{rec}} = U_{\mathrm{dip}}. \qquad (32)$$

From Table II we notice that the estimated lifetimes for all detunings are around a tenth of a second. Increasing the light intensity by an order of magnitude will increase U_{dip}, Γ_{sc} and the trapping temperature proportionally by an order of magnitude. The estimated lifetime, however, will according to Eq. (32) remain invariant.

We also note from Table II that increasing the absolute detuning from 500 GHz to 1500 GHz has a rather small effect on the estimated lifetime. This rather unexpected or irregular feature tends to stem from the fact that we do not have a two-level system, but rather a multilevel case. Increasing the detuning above 1000 GHz or lowering it below −1000 GHz rapidly brings in a contribution from the nearest vibrational levels $v' = 9$ or $v' = 7$ respectively. Thus, increasing the detuning does not bring the potential depth and scattering rate down to zero but rather leads to oscillations, as the laser frequency comes close to other vibrational resonances. Unfortunately, production of Na_2 molecules in their electronic, vibrational, and rotational ground state with 10^{-5} K temperatures seems to belong to the future. The heavier molecules Cs_2 and KRb have, however, already been produced in their rovibronic ground state [20–22].

B. The OH molecule: Trapping with laser light

As a second example we will consider the possibility of trapping an OH molecule in the lowest vibrational and rotational level of its electronic ground state. The electronic ground state of the OH molecule has a rather complex structure of energy levels due to spin-orbit coupling, Λ-doubling and magnetic hyperfine interaction. To be more specific, we will calculate the trapping force and scattering rate (lifetime) for individual hyperfine- and Zeeman levels of the lowest Λ-doublet component of the $^2\Pi_{3/2}$ substate (cf. Fig. 2). In this case there is a rather strong transition from the $X^2\Pi$ ground state to the first excited $A^2\Sigma^+$ state. The electric dipole transition element of Eq. (24) now takes the form

$$\langle X^2\Pi, v = 0 | d_{\pm 1} | A^2\Sigma^+, v' \rangle, \qquad (33)$$

and peaks strongly at $v' = 0$, with a value of 0.104 a.u. Thus, no other vibrational levels of the $A^2\Sigma^+$ state will be included in the present calculations. Bauschlicher and Langhoff [23] have presented theoretical potential curves and dipole transition moments for both these electronic states, and their results were used for the present study.

Figure 2 shows the lowest Λ-doublet of the $X^2\Pi_{3/2}$ substate, with hyperfine splittings. We consider transitions from the lowest Λ-component ($J = 3/2$, parity −) to the lowest rotational level ($N = 0$, $J = 1/2$, parity +) of the $A^2\Sigma^+$state. The resonance frequency is approximately 32 440 cm^{-1} (972 540 GHz), and the detunings introduced later are with reference to this resonance frequency. The energy gap up to the next relevant rotational level ($N = 2$, $J = 3/2$, and $J = 5/2$, parity +) is approximately 3100 GHz, which is much larger than the present detunings. Thus, excited rotational levels of the $A^2\Sigma^+$state are not included in the present calculations.

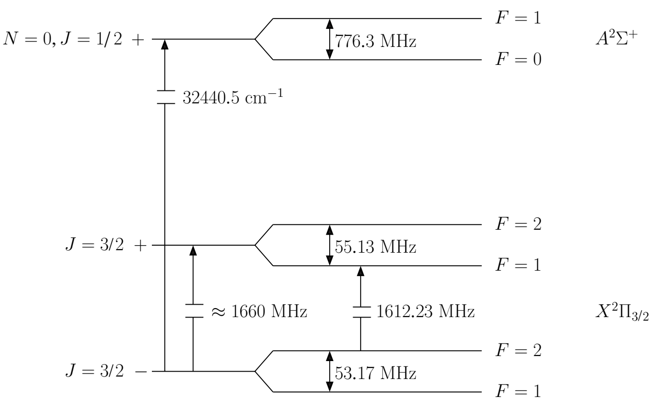

FIG. 2. Relevant energy levels for the OH molecule (not to scale).

TABLE III. Computed potential depths and scattering rates related to the electronic transition in the OH molecule. The (red) detuning is -100 GHz (cf. text). A detuning of 100 GHz would yield quite similar numerical results, except for a change of sign for Re(α), and a repulsive potential. The intensity of the laser light is set to 10^5 W cm^{-2}.

F	M_F	μ	Re(α) (a.u.)	Im(α) (a.u.)	U_{dip} (MHz)	T (K)	Γ_{sc} (s^{-1})	τ (s)
1	±1	∓1	185	2.13×10^{-4}	0.85	8.2×10^{-5}	12.3	0.29
1	±1	0	73.8	8.50×10^{-5}	0.34	3.3×10^{-5}	4.90	0.30
1	0	±1	73.8	8.50×10^{-5}	0.34	3.3×10^{-5}	4.90	0.30
1	0	0	148	1.71×10^{-4}	0.68	6.5×10^{-5}	9.85	0.29
2	±2	∓1	444	5.10×10^{-4}	2.04	2.0×10^{-4}	29.5	0.29
2	±1	∓1	111	1.27×10^{-4}	0.51	4.9×10^{-5}	7.32	0.29
2	0	±1	73.8	8.50×10^{-5}	0.34	3.3×10^{-5}	4.90	0.29
2	0	0	148	1.71×10^{-4}	0.68	6.5×10^{-5}	9.85	0.29

To compute the transition rates Γ_k for spontaneous emissions is, just as for Na$_2$, a demanding matter, as all transitions to lower accessible states of the $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ substates have to be included. However, also in this case Eq. (28) tells us that these rates will be independent of the upper state quantum numbers F and M_F. Thus, a unique lifetime can be assigned to a given rotational level (J'), irrespective of the hyperfine and Zeeman quantum numbers. Lifetimes in good agreement with experiment were calculated by Bauschlicher and Langhoff [23], and from their results we have adopted the value $\Gamma_k = 3.50 \times 10^{-11}$ a.u. $= 1.4 \times 10^6$ s^{-1}. With this common value of Γ_k real and imaginary parts of the polarizability $\alpha_{-\mu}$ of Eq. (7) were computed for a (red) detuning of -100 GHz from the resonance frequency mentioned above. Intermediate coupling actually applies to the $X^2\Pi_{3/2}$ substate [cf. Eq. (25)], and the $A^2\Sigma^+$ state is close to coupling case (b) [cf. Eq. (26)]. The depth of the dipole potential U_{dip} and the photon scattering rate Γ_{sc} were obtained from Eqs. (9) and (10) respectively, with an assumed light intensity of 10^5 W cm^{-2}. Table II also lists the temperature according to $1/2k_BT = U_{\text{dip}}$, and the lifetime τ from Eqs. (31) and (32), with $E_{\text{rec}} = 0.12$ MHz. Results for all the hyperfine and Zeeman levels are given in Table III, which also shows explicit values for all polarizations (μ) of the external light field. Negative detunings give positive values of Re(α) and, according to Eq. (6), an attractive potential.

The potential depths show a rather strong dependence on the trapping state as well as on the polarization of the laser light, ranging from around 0.3 to 2 MHz. Corresponding upper bounds for the trapping temperature are in the range 3×10^{-5} K to 2×10^{-4} K. The lifetimes are all quite similar, around 0.3 s. Increasing the red detuning by a factor of 2, i.e., to -200 GHz, would reduce the potential depth and temperature by a factor of 2 but increase the lifetime by a factor of 4, an effect that is typical for a two-level system. Cooling of OH by means of Stark deceleration [24–26] has generally led to lowest temperatures of the order of magnitude mK. This, unfortunately, tends to be an order of magnitude higher than the temperature that would enable Stark-cooled OH molecules to be loaded into and stored in an optical dipole trap, at least with lifetimes in the trap of the order of magnitude of seconds. A crucial point is, however, the intensity of the laser field, as the potential depth and temperature are proportional to the intensity, whereas the lifetime stays invariant.

C. Trapping OH by microwaves

Another possibility for trapping OH molecules might be to utilize the Λ-doubling microwave transition at about 1660 MHz (cf. Fig. 2). The small energy separation will in this case lead to a very small scattering rate, which, combined with a very small recoil energy [cf. Eqs. (31) and (32)], will lead to a virtually infinite lifetime in the trap. Fortunately, the microwave transition is quite strong, enabling considerable potential depths at modest microwave intensities. The permanent dipole moment, including the nuclear contribution, was computed to be $\langle X^2\Pi, \nu = 0 | d_0 | X^2\Pi, \nu = 0 \rangle = 0.707$ a.u. It should here be noticed that the permanent dipole moment of a polar molecule does not lead to any direct or first-order contribution to the trapping force. Its contribution vanishes due to the time averaging in the rapidly oscillating external field. Thus, the dipole potential is given by Eqs. (7) and (9) also for polar molecules. The rate for spontaneous emission

TABLE IV. Computed potential depths and scattering strengths related to the Λ-doubling microwave transitions in OH (cf. text). The detuning is -5 MHz, and the microwave intensity is set to 1 W cm^{-2}. The results given are for $\mu = 0$ (linear polarization).

Transition	Re(α) (a.u.)	Im(α) (a.u.)	U_{dip} (MHz)	Γ_{sc} (s^{-1})	T (K)	τ (s)
$F = 1 \to F' = 1$	3.40×10^8	5.25×10^{-10}	15.6	2.9×10^{-10}	1.5×10^{-3}	∞
$F = 1 \to F' = 2$	1.35×10^8	2.10×10^{-10}	6.2	1.2×10^{-10}	0.58×10^{-3}	∞
$F = 2 \to F' = 1$	8.10×10^7	1.25×10^{-10}	3.7	7.3×10^{-10}	0.36×10^{-3}	∞
$F = 2 \to F' = 2$	3.94×10^8	6.05×10^{-10}	18.1	3.5×10^{-10}	1.7×10^{-3}	∞
$2,2 \to 2,2$	8.45×10^8	1.32×10^{-9}	39.2	7.7×10^{-10}	3.8×10^{-3}	∞
$1,1 \to 1,1$	4.86×10^8	7.50×10^{-10}	22.2	4.4×10^{-10}	2.2×10^{-3}	∞
$1,1 \to 2,1$	1.78×10^8	2.74×10^{-10}	8.2	1.6×10^{-10}	0.78×10^{-3}	∞

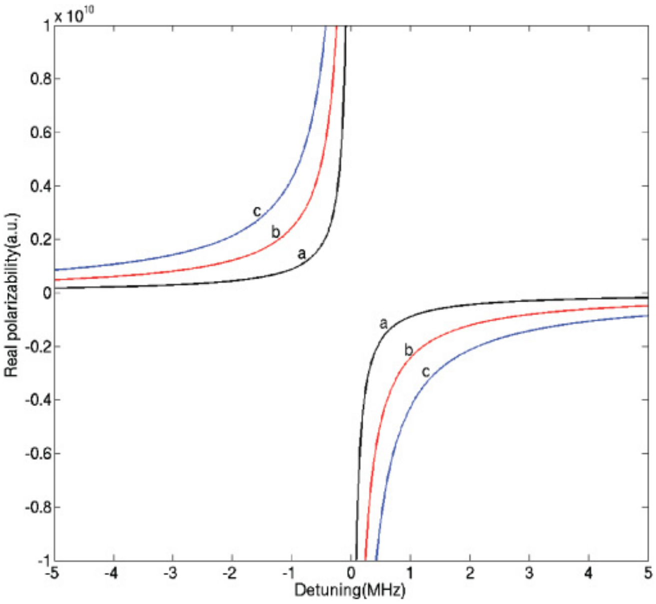

FIG. 3. (Color online) The real part of the polarizability α_0 [cf. Eq. (7)] for detunings in the range -5 to 5 MHz. The curves correspond to the transitions listed in the lowest three lines of Table IV. (a) Transition 1,1 → 2,1; (b) Transition 1,1 → 1,1; and (c) transition 2,2 → 2,2.

from the upper Λ-doublet level is easily obtained as there is just one transition to include. As in the previous examples it will be independent of the hyperfine and Zeeman quantum numbers F and M_F of the upper state, and the common value for all the relevant microwave transitions is calculated to be $\Gamma_k = 2.33 \times 10^{-27}$ a.u. $= 9.63 \times 10^{-11}$ s^{-1}.

Real and imaginary parts of the complex polarizability were calculated from Eq. (7), with the energy difference $|E_n - E_k|$ set to the relevant resonance energies as given in Fig. 2. Table IV shows the results for various transitions for a detuning of -5 MHz. The upper four rows of the table are for mixed initial states of the form $|\Psi_n\rangle = \frac{1}{\sqrt{2F+1}} \sum_{M_F=-F}^{F} |FM_F\rangle$, where F refers to the lower and F' to the upper level of the Λ doublet. The lower three entries represent examples of transitions between separate hyperfine and Zeeman states, denoted by $F, M_F \rightarrow F', M'_F$. Results are given only for linear polarization of the external field, i.e., $\mu = 0$. Inclusion of circular polarization ($\mu = \pm 1$) would add similar, although different, potential depths and scattering rates to the results presented in Table IV.

From the results of Table IV we see that a microwave intensity of 1 W cm^{-2} and a negative detuning of -5 MHz leads to considerable potential depths of up to 40 MHz and upper bounds for the trapping temperature in the range 4×10^{-4} to 4×10^{-3} K. The scattering rate $\Gamma_{\rm sc}$ is in all cases insignificant, with infinite lifetimes in the trap. As the lifetime poses no problem, deeper potentials and higher temperatures might be obtained with smaller detuning or higher microwave intensity. Thus, microwave trapping should hold a realistic potential for accommodating OH molecules precooled by Stark deceleration. The real parts of the polarizabilities $\alpha_{-\mu}$ for $\mu = 0$ are shown in Fig. 3 as a function of the detuning. For absolute detunings lower than 2 MHz there is a steep rise in the polarizabilities, and small microwave intensities will yield large potential depths. A recent successful experiment on microwave lensing of NH$_3$ molecules [27] might represent the first important step toward microwave trapping of polar molecules.

IV. CONCLUDING REMARKS

We have made a detailed study of the dipole force on a rotating diatomic molecule from an external polarized electromagnetic wave field. Our approach is based on the calculation of complex polarizabilities for individual molecular states, with specification of hyperfine as well as Zeeman quantum numbers (F and M_F). First we investigate the prospects for optical trapping of diatomic molecules by means of laser light. Our examples are the electronic, vibrational, and rotational ground states of ^{23}Na$_2$ and OH. Disregarding the small nuclear spin-spin interaction, there is no degeneracy in the ground state of Na$_2$ and consequently no individual state dependencies of the dipole force. Table II presents results for a laser intensity of 10^3 W cm^{-2} and (red) detunings in the range -500 to -1500 GHz. With this choice of parameters attractive dipole potentials with depths in the range 0.1 to 1 MHz are obtained. The upper bounds for the trapping temperatures are of order of magnitude 10^{-5} to 10^{-4} K, and trapping times are around 0.1 s.

OH with its degenerate ground state offers several interesting opportunities. Computed results for the various hyperfine and Zeeman states are listed in Table III. With a (red) detuning of -100 GHz and a laser intensity of 10^5 W cm^{-2}, we find dipole trap depths in the range 0.3–2 MHz, trapping temperatures in the range 3×10^{-5} to 2×10^{-4} K, and a trapping time around 0.3 s.

The possibility of microwave trapping of OH tends to offer the most promising prospects (cf. Table IV). In this case the lifetime in the trap is infinite, and there seems to be choices of detuning and microwave intensities that lead to very deep trapping potentials, and trapping temperatures high enough to hold OH molecules precooled, e.g., by Stark deceleration. The fact that the trapping potentials are rather strongly dependent on the specific hyperfine or Zeeman state, might offer opportunities for interesting manipulations of the molecules in the trap. One such opportunity could be to utilize OH molecules in a microwave trap as future molecular qubits.

---

[1] R. Grimm, M. Weidemüller, and Y. B. Ovchinnikov, Adv. At. Mol. Opt. Phys. **42**, 95 (2000).

[2] I. Bloch and M. Greiner, Adv. At. Mol. Opt. Phys. **52**, 1 (2005).

[3] S. Kotochigova and E. Tiesinga, Phys. Rev. A **73**, 041405(R) (2006).

[4] D. DeMille, D. R. Glenn, and J. Petricka, Eur. Phys. J. D **31**, 375 (2004).

[5] L. D. Carr and Jun Ye, New J. Phys. **11**, 055009 (May 2009).

[6] C. Lee and E. A. Ostrovskaya, Phys. Rev. A **72**, 062321 (2005).

[7] B. L. Lev, E. R. Meyer, E. R. Hudson, B. C. Sawyer, J. L. Bohn, and Jun Ye, Phys. Rev. A **74**, 061402(R) (2006).

[8] B. H. Brandsen and C. J. Joachain, *Physics of Atoms and Molecules*, 2nd ed. (Prentice Hall, London, 2003).

[9] C. J. Foot, *Atomic Physics* (Oxford University Press, Oxford, 2005).

[10] L. Veseth, Phys. Rev. A **44**, 358 (1991).

[11] G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (D. Van Nostrand, New York, 1965).

[12] D. M. Brink and G. R. Satchler, *Angular Momentum*, 3rd ed. (Clarendon Press, Oxford, 1993).

[13] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, NJ, 1960).

[14] J. T. Hougen, N.B.S. Monogr. 115 (1970).

[15] R. N. Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, J. Mol. Spectr. **46**, 37 (1973).

[16] J. M. Brown and B. J. Howard, Mol. Phys. **31**, 1517 (1976).

[17] M. Larsson, Physica Scripta **23**, 835 (1981).

[18] L. Veseth, *Institute of Physics Report Series*, 86-05 (University of Oslo, Oslo, 1986).

[19] W. J. Stevens and M. M. Hessel, J. Chem. Phys. **66**, 1477 (1977).

[20] J. G. Danzl, M. J. Mark, E. Haller, M. Gustavsson, R. Hart, J. Aldegunde, J. M. Hutson, and H. C. Nägerl, Nat. Phys. **6**, 265 (2010).

[21] K. Aikawa, D. Akamatsu, M. Hayashi, K. Oasa, J. Kobayashi, P. Naidon, T. Kishimoto, M. Ueda, and S. Inouye, Phys. Rev. Lett. **105**, 203001 (2010).

[22] K.-K. Ni, S. Ospelkaus, M. H. G. de Miranda, A. Péer, B. Neyenhuis, J. J. Zirbel, S. Kotochigova, P. S. Julienne, D. S. Jin, and J. Ye, Science **322**, 231 (2008).

[23] C. W. Bauschlicher Jr. and S. R. Langhoff, J. Chem. Phys. **87**, 4665 (1987).

[24] S. Y. T. van de Meerakker, P. H. M. Smeets, N. Vanhaecke, R. T. Jongma, and G. Meijer, Phys. Rev. Lett. **94**, 023004 (2005).

[25] S. Y. T. van de Meerakker, N. Vanhaecke, and G. Meijer, Annu. Rev. Phys. Chem. **57**, 159 (2006).

[26] A. Marian, H. Haak, P. Geng, and G. Meijer, Eur. Phys. J. D **59**, 179 (2010).

[27] H. Odashima, S. Merz, K. Enomoto, M. Schnell, and G. Meijer, Phys. Rev. Lett. **104**, 253001 (2010).