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Dipole moments and orientation polarizabilities of diatomic molecular ions for precision atomic mass measurement

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In high precision Penning trap mass spectrometry the cyclotron frequency of a polarizable ion is perturbed due to the Stark interaction with the motional electric field. For polar diatomic molecular ions, which have adjacent rotational levels of opposite parity, these shifts can be particularly large—especially for the lowest rotational levels, which are those occupied by ions stored for many hours in cryogenic Penning traps. In order to provide corrections to precision atomic mass measurements, we consider the calculation of orientation polarizabilities of CO^+ and the positive ions of the first and second row diatomic hydrides, LiH^+ to ArH^+. Dipole moments for these ions have been calculated using the restricted coupled cluster method with perturbative triples and large basis sets. Using these dipoles and an effective Hamiltonian, we have obtained rotational-state dependent polarizabilities of the open-shell diatomic ions CO^+, NH^+, OH^+, FH^+, PH^+, SH^+, and ClH^+. Results are given for those rotational levels that are significantly populated at 4.2 K, for magnetic fields up to 10 T. For the remaining first and second row hydride cations, polarizabilities at the magnetic fields of interest can be obtained from a simple formula valid for closed-shell molecules. Conversely, in cases where the polarizability shifts can be measured, our results enable experimental determination of dipole moments.

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I. INTRODUCTION

The observation of “polarizability jumps” in the cyclotron frequency of a single CO^+ ion confined for several days in a cryogenic Penning trap strikingly demonstrates that the polarizability of an ion must be taken into account in high precision atomic mass spectrometry [1]. By considering the additional radial force due to the Stark interaction between an ion of mass m in quantum state $|i\rangle$, and the $\vec{v}\times\vec{B}$ motional electric field that the ion experiences in its cyclotron motion, it can be shown that the cyclotron frequency ω_c undergoes a fractional shift [2]

$$\Delta\omega_c/\omega_c = -\alpha_{XX}(i)B^2/m, \tag{1}$$

where

$$\alpha_{XX}(i) = 2\sum_{j\neq i}\frac{|\langle j|\mu_X|i\rangle|^2}{E_j-E_i} \tag{2}$$

is the static dipole polarizability corresponding to an electric field perpendicular to the magnetic field B (which we take to be along the Z axis), and is given in terms of the electric dipole transition matrix elements and excitation energies. (We assume throughout that $\omega_c \ll |E_j-E_i|/\hbar$ so the molecule responds adiabatically to the rotation of the motional electric field. We also neglect the electric field experienced by the ion due to the electrostatic potential used to confine the ion axially. This typically has a maximum value which is a factor of 10^2-10^3 smaller than the $\vec{v}\times\vec{B}$ electric field.) For the purpose of correcting measured cyclotron frequencies in precision atomic mass measurement, Eq. (1) can be conveniently rewritten

$$\Delta\omega_c/\omega_c = -9.929\times10^{-15}(\alpha_{XX}/[\text{a.u.}])(B/[\text{T}])^2/(m/[u]), \tag{3}$$

where 1 a.u. (atomic unit) of polarizability$=(4\pi\varepsilon_0)a_0^3$ in S.I. units, a_0 is the Bohr radius, and u is the atomic mass unit. For monatomic, singly charged, positive ions, polarizabilities are usually less than 100 a.u., e.g. see Ref. [3], and for higher states of ionization they are generally smaller. For typical Penning trap magnetic fields of 5–10 T the cyclotron frequency shifts are hence at or below the 10^{-12} level, and so are negligible at current mass measurement precision [4]. However, for molecular ions with body-frame dipole moments there can be large electric dipole matrix elements between adjacent rotational levels which have separations of order 10 cm^{-1} or less. This can lead to (orientation) polarizabilities as large as 10^4 or 10^5 a.u., and fractional cyclotron frequency shifts of order 10^{-9}. Such shifts are detectable by several Penning trap mass spectrometers that achieve relative mass measurement precision from 10^{-10} to 10^{-11} [5–8]. These spectrometers use single ions, often trapped for several days, in ultrahigh vacuum, surrounded by electrodes at 4.2 K. In this environment the diatomic ions we consider are in their lowest electronic and vibrational states, and, depending on the size of the rotational constant, predominantly in the lowest one, two or three rotational states. Due to radiative decay, and also absorption and stimulated emission of black-body radiation from the Penning trap electrodes, the ions can undergo transitions between these levels on time scales of minutes to many days. This explains the jumps in

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the cyclotron frequency observed in Ref. [1].

Molecular ions are convenient for determining atomic mass ratios precisely because they enable comparisons of cyclotron frequencies between ions of the same total mass number, and hence similar mass, typically with $\Delta m/m < 10^{-3}$. Higher accuracy is obtained since the ions then have similar motions in the Penning trap, leading to a large reduction in most systematic errors [9]. (Individual atomic masses are obtained from a least squares adjustment using sufficient independent ratios that the unknown atomic masses can be related to ^{12}C. Corrections for the mass equivalent of the molecular binding energy can be made with adequate precision using known heats of formation.) In the case of the extremely high precision technique used in Ref. [1], where the cyclotron frequency ratio of the trapped ions was measured to $\pm 7 \times 10^{-12}$, the use of ions of similar mass is essential. The technique involves positioning the two ions in a stable, coupled magnetron orbit, with a separation of about 1 mm [5]. The two ions' magnetron frequencies are only sufficiently close to allow such coupling if the ions have very similar masses.

Hydride ions are important in that they enable precise mass comparison between neighboring isotopes by measuring mass ratios $M[^{A}X\mathrm{H}^+]/M[^{A+1}X^+]$, making use of the accurately known mass of the proton [10]. In turn, with knowledge of the proton-neutron mass difference [11], this enables accurate determination of the mass equivalent of neutron binding energies. Since neutron binding energies can also be determined using precision Bragg diffraction spectroscopy of the gamma-rays emitted in neutron capture, the comparison provides an important crosscheck of the two metrological techniques. In particular, measurements of the mass ratios $^{28}\mathrm{SiH}^+/^{29}\mathrm{Si}^+$ and $^{32}\mathrm{SH}^+/^{33}\mathrm{S}^+$ have been compared with wavelengths of the gamma rays from neutron capture by ^{28}Si and ^{32}S [12,13]. The comparison can also be viewed as a test of Einstein's mass energy relation, "$E=mc^2$."

In what follows, we first present results of *ab initio* calculations of the dipole moments of CO$^+$ and of the positive ions of the hydrides of the first and second rows of the periodic table. We then give a simple formula for obtaining the orientation polarizabilities of closed-electron-shell ($^1\Sigma^+$), diatomic molecules, such as CH$^+$, NeH$^+$, SiH$^+$, and ArH$^+$, in terms of the dipole moments. Following this, we present detailed results of calculations using an effective Hamiltonian method, of the polarizabilities for the open-shell diatomics CO$^+$, OH$^+$, SH$^+$, FH$^+$, ClH$^+$, NH$^+$, and PH$^+$, at fields from 0 to 10 T. These ions have $^2\Sigma^+$, $^3\Sigma^-$, $^2\Pi_{3/2}$, and $^2\Pi_{1/2}$ electronic states, respectively. The example of CO$^+$ shows that the closed-shell formula is also applicable to calculating polarizability of the other $^2\Sigma$ molecules (LiH$^+$, BH$^+$, NaH$^+$, AlH$^+$) in high magnetic fields. These ions were chosen for study because of their special relevance to precision mass measurements. However they also exemplify the most commonly encountered electronic states, and hence the calculation of polarizability, of all the lighter diatomic molecular ions. The dipole moments and molecular parameters compiled here may also be useful for other studies with cold molecular ions, e.g. see Ref. [14], and to astrophysics.

II. ORIENTATION POLARIZABILITIES

The static dipole polarizability given by Eq. (2) in general involves summation over all rotational, vibrational and electronic states. Including only the rotational states within the lowest vibrational and electronic state gives the "orientation polarizability." This contribution can be thought to arise from the progressive alignment of the body frame dipole μ with the external electric field. This contribution is proportional to μ^2 and is zero for homonuclear molecules. The contribution from different vibrational and electronic states corresponds to a redistribution of charge of the nonrotating molecule and can be called the "distortion polarizability." In a gas at room temperature the orientation polarizability is given by the classical result $\alpha=\mu^2/3kT$ and is comparable in magnitude with the distortion polarizability [15]. However in the 4.2 K environment of the Penning trap, where only the lowest rotational levels are populated, the orientation contribution can be much larger. This is the only contribution evaluated here. We note that for H$_2^+$ and its isotopomers HD$^+$, HT$^+$, etc., total static polarizabilities have been calculated *ab initio* by solving the three-body Schrödinger equation using highly accurate variational methods, e.g., see Refs. [16,17]. For H$_2^+$ and D$_2^+$, accurate polarizabilities have also been obtained experimentally, using microwave spectroscopy of Rydberg H$_2$ and D$_2$ [18].

A. Electric dipole moments

We have calculated the near equilibrium parts of the dipole moment functions of CO$^+$ and the first and second row hydride cations and hence obtained dipole moments corresponding to the lowest vibrational state. These calculations were performed with the MOLPRO program suite [19], the nuclear motion problem being solved using the Cooley method [20]. We used the restricted coupled cluster method with perturbative triples [RCCSD(T)] and large basis sets: from C to Ne and Si to Ar augmented correlation-consistent polarized valence of quintuple zeta quality (aug-cc-pV5Z), for Li and Na correlation-consistent polarized core-valence quadruple zeta (cc-pCVQZ), for Be, B, Mg, Al cc-pV5Z. For Li, Be, and B all electrons were correlated, for Na, Mg, and Al core-core and core-valence correlation with the lower shell were included. The electric dipole moments relative to the center of mass were obtained from the RCCSD(T) energies corresponding to applied fields of ±0.005 a.u.

The calculated dipoles and internuclear separations for the ground vibrational state (zero-point separations) are shown in Table I. Some previous theoretical values for the dipole moments, in some cases obtained from tabulated dipole moment functions, are also shown. The table also gives experimental values for the rotational constants, and, for comparison with the theoretical values, the corresponding experimental zero-point separations (except for ^{7}LiH$^+$ and ^{23}NaH$^+$ where no experimental data was found). Based on our experience with these calculations we estimate the uncertainty in the dipoles to be $\pm 0.008 e a_0$. The dipole moment functions close to equilibrium, which are important for determining vibrational transition rates, are shown in Figs. 1 and 2.

TABLE I. Calculated electric dipole moments μ_0, and internuclear separations R_0, for the lowest vibrational state of CO^+ and the hydride cations LiH^+ to ArH^+. Some previous theoretical results for the dipole moments, and experimentally determined rotational constants B_0 and corresponding experimental R_0 are also shown. A positive sign for the dipole implies it is directed towards the lighter nucleus. μ_0 and R_0 are given in atomic units (ea_0, a_0), B_0 is given in cm^{-1}.

Diatomic ion	State	μ_0 (This work)	μ_0 (Other)	R_0 (This work)	R_0 (Expt.)	B_0 (Expt.)
$^{12}C^{16}O^+$	$^2\Sigma^+_{1/2}$	1.0352	1.015 [21][a]	2.1160	2.1125	1.9675 [29]
$^7LiH^+$	$^2\Sigma^+_{1/2}$	−0.3049		4.2729		(3.7416)[d]
$^9BeH^+$	$^1\Sigma^+_0$	−1.1646	−1.168 [23]	2.4838	2.4944	10.674 [30]
$^{11}BH^+$	$^2\Sigma^+_{1/2}$	0.1673		2.2814	2.2957	12.371 [31]
$^{12}CH^+$	$^1\Sigma^+_0$	0.6623	0.6516 [24][b]	2.1530	2.1559	13.930 [32]
$^{14}NH^+$	$^2\Pi_{1/2}$	0.7897		2.0406	2.0437	15.331 [33]
$^{16}OH^+$	$^3\Sigma^-_{0,1}$	0.9134		1.9641	1.9663	16.422 [34]
$^{19}FH^+$	$^2\Pi_{3/2}$	1.0438		1.9157	1.9168	17.119 [35]
$^{20}NeH^+$	$^1\Sigma^+_0$	1.1823		1.9022	1.9023	17.338 [36]
$^{23}NaH^+$	$^2\Sigma^+_{1/2}$	−0.0485		5.0991		(2.3980)[d]
$^{24}MgH^+$	$^1\Sigma^+_0$	−1.3293		3.1494	3.1442	6.296 [37]
$^{27}AlH^+$	$^2\Sigma^+_{1/2}$	−0.1428		3.0512	3.0769	6.545 [38]
$^{28}SiH^+$	$^1\Sigma^+_0$	0.1714		2.8644	2.8617	7.5566 [39]
$^{31}PH^+$	$^2\Pi_{1/2}$	0.3424		2.7136	2.7118	8.3868 [40]
$^{32}SH^+$	$^3\Sigma^-_{0,1}$	0.5139	0.508 [26]	2.5988	2.5974	9.1333 [41]
$^{35}ClH^+$	$^2\Pi_{3/2}$	0.6887	0.669 [27]	2.5071	2.5055	9.7819 [42]
$^{40}ArH^+$	$^1\Sigma^+_0$	0.8566	0.7587 [28][c]	2.4430	2.4416	10.273 [43]

[a] Also 1.09 [22].

[b] Also 0.6606 [25].

[c] μ_e, for other values see text.

[d] Obtained from the theoretical R_0.

In each case the dipoles have been calculated for the most abundant isotopes. Dipoles for other isotopes can be obtained by correcting for the change in position of the center of mass under the approximation that neither the internuclear separation nor position of the center of charge changes. The change in dipole, in the sense directed from nucleus 1 to nucleus 2, is then given by

$$\Delta\mu = eR \times \Delta[m_1/(m_1 + m_2)], \tag{4}$$

where e is the unit of charge, R is the internuclear separation and m_1, m_2 are the nuclear masses. Equation (4) can also be used to estimate the small dipole moments of homoatomic but nonhomonuclear molecules such as $^{14}N^{15}N^+$.

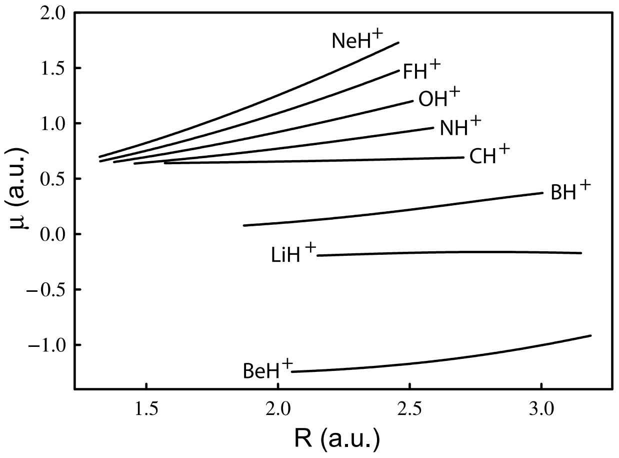

FIG. 1. Dipole moment as a function of internuclear separation: LiH^+ to NeH^+.

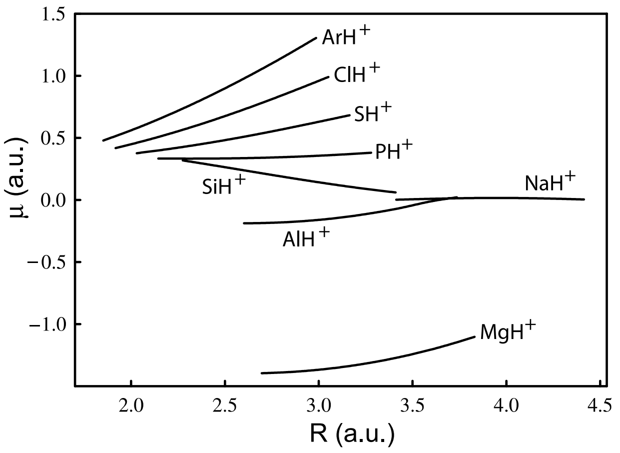

FIG. 2. Dipole moment as a function of internuclear separation: NaH^+ to ArH^+.

Electric dipole moments of molecular ions are required for determining rotational line strengths and decay rates, and have many applications in astrophysics and studies of ion-molecule reactions. Prior to the measurement of polarizability shifts of CO^+ in Ref. [1], experimental determinations of dipole moments in diatomic molecular ions have been based on isotopic substitution in the rotational Zeeman effect [44–46], or else extensive analysis of pure-rotation and vibration-rotation spectra of isotopic variants [47]. The example of ArH^+, which has received most attention, shows the difficulties with these previous experimental methods. The experimentally determined dipole moments of 1.4(0.4) D [44] and 3.0(0.6) D [45] may be compared with early *ab initio* calculations giving 2.384 D [48], 2.1(0.1) D [49], 2.215 D [50], a more recent theoretical result of 1.9283 D [28], our result of 2.177 D in Table I and the recent experimental determination from detailed spectral analysis 2.12(0.55) D [47] ($1\ ea_0=2.541\ 58$ D). Similarly, the experimental value for KrH^+ is 3.0 D [46] versus a theoretical prediction of 1.944 D [51].

B. Polarizability of closed-shell diatomic molecules

For diatomic molecules with closed-electron-shell ($^1\Sigma^+$) electronic ground states, the lowest rotational levels are given to first order by the rigid-rotor expression $E_J=B_0J(J+1)$. Using standard results for the direction cosines relating the molecular frame to the laboratory frame [52], the dipole polarizability corresponding to an electric field oriented perpendicular to the quantization axis is found to be

$$\alpha_{XX}(J,M_J)=\frac{J(J+1)-3M_J^2}{2J(J+1)(2J-1)(2J+3)}\frac{\mu^2}{B_0}, \tag{5}$$

for $J\neq 0$, and

$$\alpha_{XX}(0)=\frac{\mu^2}{3B_0}, \tag{6}$$

for $J=0$, where J and M_J are the rotational quantum number and its projection on the laboratory-fixed Z axis, μ is the (body-frame) molecular dipole moment, and B_0 is the rotational constant of the molecule in its ground-electronic and vibrational state. We note that here, for $J\neq 0$, $\alpha_{XX}=-\alpha_{ZZ}/2$, while for $J=0$, $\alpha_{XX}=\alpha_{ZZ}$, where α_{ZZ} is the more usual electric polarizability for an electric field parallel to the quantization axis [52]. The average of the polarizability over all M_J states is zero for $J\neq 0$, but not for $J=0$, in accord with the reduced orientation polarizability of molecules at higher temperature. As an example, for the closed-shell molecule $^{28}SiH^+$ the data in Table I and Eq. (6) give a ground-state polarizability of 285 a.u. At the 8.53 T field used in Ref. [13], this implies a cyclotron frequency shift of −7.1 ppt, which is comparable with the error of that measurement. For the metrologically and astrophysically important ion $^{12}CH^+$, the ground state polarizability and corresponding cyclotron frequency shift at 8.53 T are certainly significant: 2304 a.u. and −128 ppt, respectively. For HeH^+ ($B_0=1006.06$ GHz [53], $\mu=0.67245ea_0$ [54]), $\alpha=986$ a.u., and the frequency shift is −142 ppt.

C. Polarizability of open-shell diatomic molecules

For diatomic molecules having nonzero electronic angular momenta, Eq. (2) can be evaluated using energies and transition matrix elements obtained by solving the Schrödinger equation based on an effective Hamiltonian [55], using molecular parameters obtained from fits to experimental spectroscopic data. In the present work, we obtained orientation polarizabilities using codes developed for determining rotational energies and line strengths for the analysis of laser magnetic resonance spectra [56], based on the effective Hamiltonian described in Refs. [57,58]. The molecular parameters used are given in Tables IX–XV of the Appendix. In some instances full sets of experimental parameters were not available, in which case the remaining parameters were estimated. Because the Zeeman effect can shift and mix rotational levels, the polarizabilities are in general magnetic-field dependent. The calculations necessarily involve extrapolation from the lower fields at which the Zeeman parameters were determined. In some cases the polarizabilities exhibit large anomalies due to level crossings. Near such crossings sensitivity to the molecular parameters can be greatly enhanced.

For the relatively low-Z hydride cations considered here, at the magnetic fields of interest for precision mass measurement, the Zeeman interactions with the external field are generally much larger than any internal hyperfine interactions. This causes the proton spin, and any other nuclear spins, to be effectively decoupled from the other molecular angular momenta. The result is that in general we can neglect hyperfine effects on the polarizability. The exception is $^{31}PH^+$ where the Zeeman effect is very small for the $J=1/2$ level and the hyperfine interaction involving the ^{31}P spin is quite large. In this case we have included the relevant hyperfine interaction in the effective Hamiltonian.

D. State-dependent molecule-fixed polarizability contribution

Although negligible at current mass measurement precision, the "distortion" contribution to the polarizability of a diatomic molecule, in Hund's case (a) rotational state J, Ω, M_J, with electric field perpendicular to the quantization axis, can be obtained from

$$\begin{aligned}\alpha_{XX}(J,\Omega,M_J)=&\frac{1}{3}(2\alpha_\perp+\alpha_\parallel)\\&-\frac{[3M_J^2-J(J+1)][3\Omega^2-J(J+1)]}{3J(J+1)(2J-1)(2J+3)}\\&\times(\alpha_\parallel-\alpha_\perp),\end{aligned} \tag{7}$$

where $\alpha_\perp=\alpha_{xx}=\alpha_{yy}$, and $\alpha_\parallel=\alpha_{zz}$ are the body-frame polarizabilities. For a molecule corresponding to Hund's case (b), the quantum numbers J, Ω, and M_J can be replaced by N, Λ, and M_N. As specific examples, for HeH^+ [59], this contributes only 1.92 a.u. to the polarizability of the ground rotational level, for CO^+ [21] it contributes 8.47 a.u.

TABLE II. Polarizability α_{XX} of $^{12}C^{16}O^+$, $X\ ^2\Sigma^+$, $v=0$, $N=0, 1, 2$, $B=0-10$ T.

N	J	M_J	0	2	4	6	8	10	8.5294	CS[a]
0	1/2	−1/2	39848	39844	39841	39839	39836	39833	39836	39846
		+1/2	39844	39849	39852	39853	39856	39858	39856	39846
1	1/2	−1/2	541	11953	11951	11953	11952	11951	11952	11953
		+1/2	−550	−5991	−5989	−5987	−5984	−5982	−5984	−5977
	3/2	−3/2	−5959	−5959	−5959	−5959	−5958	−5958	−5958	−5977
		−1/2	5421	−5996	−5999	−6001	−6004	−6006	−6005	−5977
		+1/2	6508	11955	11955	11955	11956	11957	11956	11953
		+3/2	−5959	−5960	−5960	−5960	−5960	−5960	−5960	−5977
2	3/2	−3/2	−1938	1425	1425	1425	1425	1426	1426	1423
		−1/2	2017	2846	2845	2845	2844	2844	2845	2846
		+1/2	1962	1422	1422	1422	1423	1423	1423	1423
		+3/2	−2050	−2849	−2849	−2848	−2848	−2848	−2848	−2846
	5/2	−5/2	−2842	−2842	−2842	−2842	−2842	−2842	−2842	−2846
		−3/2	514	−2850	−2850	−2851	−2851	−2852	−2851	−2846
		−1/2	2250	1421	1421	1420	1420	1420	1420	1423
		+1/2	2306	2847	2848	2848	2849	2849	2849	2846
		+3/2	626	1425	1425	1425	1425	1425	1425	1423
		+5/2	−2842	−2842	−2842	−2842	−2842	−2842	−2842	−2846

[a] Closed-shell result from Eqs. (5) and (6).

III. RESULTS OF THE ORIENTATION POLARIZABILITY CALCULATIONS

Tables II–VIII give the results of the polarizability calculations using the effective Hamiltonian and the dipole moments given in the third column of Table I. Polarizabilities are tabulated for the lowest three rotational levels of CO$^+$, and for the lowest two rotational levels of the hydride cations OH$^+$, SH$^+$, FH$^+$, ClH$^+$, NH$^+$, and PH$^+$, for fields from 0 to 10 T, and also for the field of 8.5294 T as used in Refs. [1,13]. Figures 3–9 give the corresponding Zeeman diagrams. In the following we discuss these results, and the consequences for precision mass measurement, case by case.

A. CO$^+$

This molecular ion has a $^2\Sigma^+$ ground state and is well described by Hund's coupling case (b) [60]. Due to the unpaired electron spin it exhibits a large Zeeman effect, see

TABLE III. Polarizability α_{XX} (a.u.) of OH$^+$, $X\ ^3\Sigma^-$, $v=0$, $N=0, 1$, $B=0-10$ T.

N	J	M_J	0	2	4	6	8	10	8.5294	CS[a]
0	1	−1	3779	3778	3778	3777	3777	3776	3776	3716
		0	3613	3613	3613	3613	3613	3613	3613	3716
		1	3779	3781	3783	3785	3789	3794	3790	3716
1	0	0	−247	−468	−610	−635	−638	−640	−638	−557
	1	−1	255	817	996	1054	1079	1091	1083	1115
		0	537	805	1000	1053	1070	1078	1073	1115
		1	254	−277	−426	−468	−483	−490	−486	−557
	2	−2	−592	−592	−592	−592	−592	−592	−592	−557
		−1	373	−189	−369	−427	−452	−465	−456	−557
		0	−370	−418	−471	−501	−518	−529	−521	−557
		1	373	905	1054	1096	1112	1119	1114	1115
		2	−592	−592	−591	−591	−591	−591	−591	−557

[a] Closed-shell result from Eq. (5) and (6).

TABLE IV. Polarizability α_{XX} (a.u.) of SH$^+$, $X\,^3\Sigma^-$, $v=0$, $N=0$, 1, $B=0$–10 T.

N	J	M_J	0	2	4	6	8	10	8.5294	CS[a]
0	1	−1	2407	2372	2349	2333	2321	2312	2318	2115
		0	1852	1853	1855	1858	1863	1871	1865	2115
		1	2407	2465	2577	2862	4811	718	12832	2115
1	0	0	−918	−959	−1083	−1376	−3316	795	−11332	−317
	1	−1	101	236	345	416	458	481	466	−317
		0	266	319	420	499	540	556	547	−317
		1	101	−18	−93	−131	−150	−158	−152	635
	2	−2	−395	−396	−397	−398	−399	−400	−399	−317
		−1	406	268	154	78	29	−2.5	19	635
		0	178	143	79	27	−5.9	−19	−11	635
		1	406	529	607	649	671	683	674	−317
		2	−395	−394	−393	−391	−388	−385	−387	−317

[a] Closed-shell result from Eqs. (5) and (6).

Fig. 3, which for magnetic fields above ~0.04 T leads to almost complete decoupling of the electron spin from the molecular rotation. The rotational states then split into two independent "closed-shell" manifolds, corresponding to the components of electron spin $M_S=\pm 1/2$. The polarizabilities hence become independent of magnetic field strength, see Table II. It is interesting to note that there is a crossing between substates of the $N=0$ and $N=1$ levels just above 4 T, and of the $N=1$ and $N=2$ levels near 8.5 T. These crossings involve levels of opposite parity. However, except very close to the crossing fields, this does not produce any anomalies in the polarizabilities because the electron spin is almost fully decoupled at these magnetic fields, and the electric dipole matrix element obeys the selection rule $\Delta M_S=0$.

The approximation that the polarizabilities are given by an expression equivalent to Eqs. (5) and (6), was made in the

TABLE V. Polarizability α_{XX} (a.u) of FH$^+$, $X\,^2\Pi_{3/2}$, $v=0$, $J=3/2$, 5/2, $B=0$–10 T.

J	Parity	M_J	0	2	4	6	8	10	8.5294
3/2	−	−3/2	1.695×10^{6}	67189	34640	23496	17865	14467	16812
		−1/2	3.953×10^{6}	17222	10662	7743	6146	5143	5838
		+1/2	3.953×10^{6}	−28818	−12325	−7572	−5333	−4033	−4926
		+3/2	1.695×10^{6}	−71287	−34496	−22568	−16663	−13137	−15567
	+	−3/2	-1.693×10^{6}	73017	36130	24172	18251	14717	17153
		−1/2	-3.952×10^{6}	30588	14019	9238	6985	5676	6575
		+1/2	-3.952×10^{6}	−15796	−9140	−6191	−4579	−3568	−4269
		+3/2	-1.693×10^{6}	−65804	−33179	−22007	−16362	−12955	−15306
5/2	+	−5/2	1.316×10^{5}	32395	18656	13188	10251	8417	9687
		−3/2	3.423×10^{5}	−12394	3618	4440	4101	3661	3983
		−1/2	4.477×10^{5}	−43520	−7952	−2600	−970	−314	−740
		+1/2	4.477×10^{5}	−61685	−16346	−8126	−5101	−3619	−4615
		+3/2	3.423×10^{5}	−67531	−21829	−12299	−8407	−6337	−7744
		+5/2	1.316×10^{5}	−61659	−24628	−15248	−10969	−8519	−10199
	−	−5/2	-1.316×10^{5}	64234	26163	16560	12184	9680	11397
		−3/2	-3.420×10^{5}	69486	22752	12952	8931	6786	8244
		−1/2	-4.472×10^{5}	61851	16349	8055	4988	3480	4495
		+1/2	-4.472×10^{5}	41989	7248	2074	521	−92.34	306
		+3/2	-3.420×10^{5}	10521	−4287	−4812	−4334	−3816	−4192
		+5/2	-1.316×10^{5}	−31952	−18007	−12447	−9457	−7591	−8884

TABLE VI. Polarizability α_{XX} (a.u.) of ClH$^+$, $X\,^2\Pi_{3/2}$, $v=0$, $J=3/2$, $5/2$, $B=0-10$ T.

J	Parity	M_J	0	2	4	6	8	10	8.5294
3/2	−	−3/2	8.896×10^{6}	32794	16655	11257	8552	6925	8048
		−1/2	2.076×10^{7}	11203	6000	4232	3340	2800	3173
		+1/2	2.076×10^{7}	−10407	−4791	−2949	−2031	−1482	−1861
		+3/2	8.896×10^{6}	−32068	−15750	−10318	−7600	−5967	−7094
	+	−3/2	-8.895×10^{6}	33041	16719	11286	8568	6935	8062
		−1/2	-2.076×10^{7}	11763	6141	4294	3374	2822	3203
		+1/2	-2.076×10^{7}	−9871	−4664	−2895	−2003	−1465	−1837
		+3/2	-8.895×10^{6}	−31845	−15699	−10298	−7590	−5961	−7085
5/2	+	−5/2	6.824×10^{5}	21669	11159	7580	5775	4686	5438
		−3/2	1.774×10^{6}	11417	6212	4277	3274	2661	3084
		−1/2	2.320×10^{6}	1912	1541	1152	908	747	860
		+1/2	2.320×10^{6}	−6882	−2862	−1794	−1313	−1041	−1228
		+3/2	1.774×10^{6}	−14999	−7004	−4554	−3371	−2677	−3155
		+5/2	6.823×10^{5}	−22464	−10884	−7107	−5233	−4113	−4886
	−	−5/2	-6.823×10^{5}	23165	11548	7759	5878	4754	5530
		−3/2	-1.774×10^{6}	15246	7193	4720	3527	2825	3308
		−1/2	-2.320×10^{6}	6812	2768	1693	1209	936	1123
		+1/2	-2.320×10^{6}	−2087	−1689	−1289	−1039	−873	−989
		+3/2	-1.774×10^{6}	−11410	−6144	−4190	−3178	−2562	−2987
		+5/2	-6.823×10^{5}	−21104	−10563	−6973	−5162	−4071	−4825

analysis of the precise mass comparison of CO$^+$ to N$_2^+$ by Thompson *et al.* in Refs. [1,2]. Treating the dipole moment as an unknown, they obtained an experimental value of $\mu=1.025(15)ea_0$ from cyclotron frequency shifts between the $N=0$, and $N=1$, $M_N=0,\pm1$ states. This agrees with the earlier theoretical value of $1.015ea_0$, obtained using a CASSCF calculation [21] and with our theoretical value of $1.035(8)ea_0$, see Table I. The close agreement between the polarizabilities in the last two columns in Table II, which are obtained from the full effective Hamiltonian, and from the closed-shell formula, respectively, indicates that this simplified analysis is indeed correct at the 0.1% level. In Ref. [2] it was also shown that if a more accurate value of the dipole moment of CO$^+$ could be obtained independently, one could use the measured cyclotron frequency ratio for the well resolved, and most precisely measured $N=0$ state, to obtain an improved value for the mass ratio $R=M[\mathrm{CO}^+]/M[\mathrm{N}_2^+]$, using $R=0.999\,598\,888\,635(7)-959\times10^{-12}(\mu/ea_0)^2$. Our de-

TABLE VII. Polarizability α_{XX} (a.u.) of NH$^+$, $X\,^2\Pi_{1/2}$, $v=0$, $J=1/2$, $3/2$, $B=0-10$ T.

J	Parity	M_J	0	2	4	6	8	10	8.5294
1/2	+	−1/2	131895	131204	130261	128737	126342	122884	125538
		+1/2	131895	132702	134006	136223	139837	145493	141101
	−	−1/2	−128921	−129727	−131028	−133241	−136850	−142499	−138112
		+1/2	−128921	−128229	−127284	−125756	−123356	−119892	−122551
3/2	−	−3/2	24053	8510	4855	3216	2281	1672	2096
		−1/2	57034	−19991	−1212	747	1244	1402	1304
		+1/2	57034	−38591	−7484	−3223	−1705	−966	−1462
		+3/2	24054	−40792	−12094	−7443	−5537	−4500	−5207
	+	−3/2	−24533	32221	8766	4723	3038	2108	2744
		−1/2	−56345	39932	9094	4958	3502	2796	3271
		+1/2	−56345	28768	4730	2142	1394	1095	1290
		+3/2	−24533	−9647	−6276	−4783	−3941	−3399	−3775

TABLE VIII. Polarizability α_{XX} (a.u.) of PH$^+$, $X\ ^2\Pi_{1/2}$, $v=0$, $J=1/2$, $3/2$, $B=0-10$ T. F, M_F and M_I correspond to hyperfine interaction involving the nuclear spin of ^{31}P only.

J	Parity	F	M_F	0	2	4	6	8	10	8.5294
1/2	+	0	0	27011	26951	26888	26815	26727	26616	26700
		1	−1	24435	24330	24327	24361	24420	24505	24440
			0	23988	24093	24101	24075	24030	23964	24015
			+1	27011	27072	27143	27229	27338	27476	27371
	−	0	0	−23276	−23307	−23345	−23394	−23461	−23550	−23482
		1	−1	−29101	−23098	−23230	−23426	−23663	−23928	−23731
			0	−23276	−23246	−23213	−23172	−23118	−23047	−23101
			+1	−23051	−29055	−28931	−28748	−28530	−28293	−28469
J	Parity	M_J	M_I							
3/2	−	3/2	−1/2	1426	1250	1103	978	871	778	845
			+1/2	2229	1310	1143	1011	898	801	871
		−1/2	−1/2	2910	3578	3603	3711	3945	4384	4036
			+1/2	3882	3650	3712	3870	4181	4761	4301
		+1/2	−1/2	3562	3878	4077	4408	4968	5484	5304
			+1/2	3030	3753	4000	4350	4863	5642	5037
		+3/2	−1/2	2109	1759	2033	2409	2950	3209	3166
			+1/2	1426	1640	1903	2236	2667	3247	2804
	+	−3/2	−1/2	−1557	−1695	−1875	−2120	−2469	−3007	−2588
			+1/2	−2181	−1924	−2077	−2361	−2856	−3316	−3174
		−1/2	−1/2	−2892	−3375	−3594	−3888	−4335	−5030	−4489
			−1/2	−3337	−3664	−3793	−4078	−4590	−4918	−4813
		+1/2	−1/2	−3677	−3441	−3600	−3843	−4214	−4779	−4342
			+1/2	−2891	−3247	−3505	−3727	−4052	−4538	−4162
		+3/2	−1/2	−2182	−1721	−1469	−1366	−1294	−1237	−1278
			+1/2	−1557	−1449	−1362	−1291	−1232	−1183	−1218

tailed effective Hamiltonian calculations yield a correction of $-959.5\times10^{-12}(\mu/ea_0)^2$, in complete agreement. Using our calculated dipole this gives $R=0.999\,598\,887\,607(15)$, which is slightly lower than the final result obtained from the global fit to all the cyclotron frequencies of Ref. [1], $R=0.999\,598\,887\,627(15)$. As it is difficult to specify the accuracy of our dipole moment calculations below the 1% level, we are hence unable to improve on the accuracy of the final value for this mass ratio. The importance of this ratio is that it links the atomic mass of ^{14}N to the accurately measured atomic mass of ^{16}O [61,62].

The Zeeman structure exhibited by CO$^+$ is typical of other diatomic molecules with $^2\Sigma^+$ ground states. Consequently, we can use the closed-shell expression to predict accurate polarizabilities of the lowest rotational levels, at the high magnetic fields of interest, for the hydride cations LiH$^+$, BH$^+$, NaH$^+$, AlH$^+$. The larger B_0 values for these molecules imply that the ion will predominantly occupy $N=0$.

B. OH$^+$ and SH$^+$

OH$^+$ and SH$^+$ have $^3\Sigma^-$ electronic ground states and are well described by Hund's case (b) coupling scheme. The unpaired electron spins exhibit a large Zeeman effect tending to uncouple the spin and rotational angular momenta, see Figs. 4 and 5. However, the spin-spin interaction present in $^3\Sigma$ states results in a much stronger coupling between spin and rotation than for $^2\Sigma$. For $N=1$ the residual coupling is still significant up to several tesla, particularly for SH$^+$, which has a larger spin-spin coupling parameter and smaller rotational constant, see Tables X and XI.

The calculated polarizabilities are given in Tables III and IV. For OH$^+$ these are quite similar to those obtained from the closed-shell expression, but for SH$^+$ this is less true. In fact for SH$^+$, due to the crossing of the $N=0$, $M_J=1$ and the $N=1$, $M_J=0$ levels at about 8.704 T, there are anomalously large polarizabilities for these two states at the field of 8.529 38 T that was used in the measurement of the mass ratio ^{32}SH$^+$/^{33}S$^+$ in Ref. [13]. The results for SH$^+$ presented here, which reproduce our earlier calculations used in Ref. [13], imply significant fractional cyclotron frequency shifts of the $N=0$, $M_J=-1,0,1$ states at 8.53 T of $-5.0(1)\times10^{-11}$, $-4.0(1)\times10^{-11}$, and $-2.75(4)\times10^{-10}$, respectively.

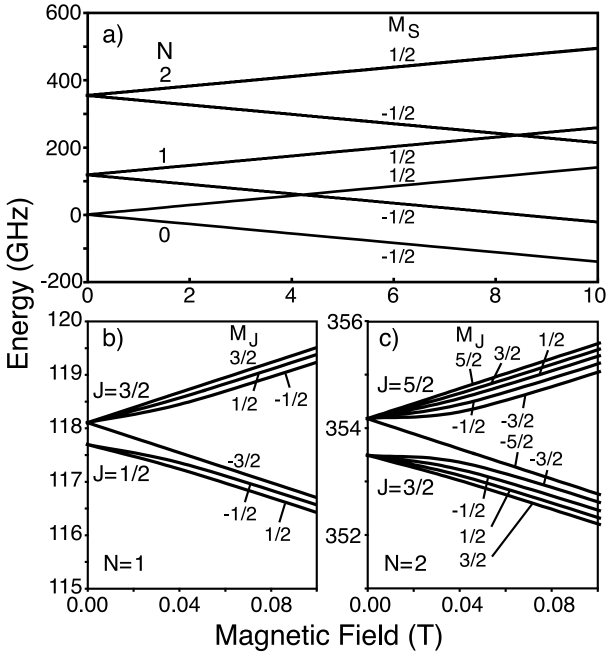

FIG. 3. Zeeman energies of CO^+, $X\,^2\Sigma^+$ ($v=0$): (a) $N=0,1,2$, for $B=0-10$ T, (b) $N=1$, $B=0-0.1$ T, (c) $N=2$, $B=0-0.1$ T.

C. FH^+ and ClH^+

FH^+ and ClH^+ have $^2\Pi_{3/2}$ ground electronic states well described using the Hund's (a) coupling scheme and exhibit large Zeeman splittings, see Figs. 6 and 7. Each J, M_J level consists of a very closely spaced pair of opposite parity lambda-doubling components, unresolved in the figures. However, the motional electric field is rigorously perpendicular to the quantization axis, and the largest contribution to the polarizability comes from dipole matrix elements between neighboring Zeeman levels according to the selection rule $\Delta M_J = \pm 1$. This leads, at high magnetic field, to a decrease in the polarizability with increasing B, and also, for $J=3/2$, to similar polarizabilities for both parity components of given M_J, as can be seen in Tables V and VI. For both FH^+ and ClH^+, matrix elements with $\Delta\Omega = \pm 1$ made insignificant contribution to the polarizabilities. This is because the two spin components are widely separated in energy and because of the $\Delta\Sigma = 0$ selection rule in the Hund's case (a) limit. (However the full basis set was used to calculate the energy levels of all the $^2\Pi$ molecules in a magnetic field).

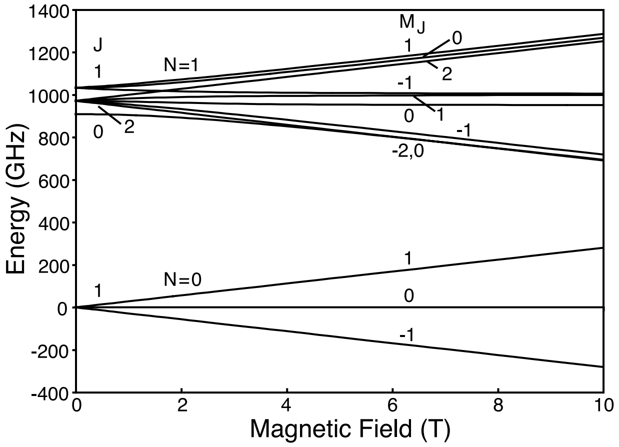

FIG. 4. Zeeman energies of OH^+, $X\,^3\Sigma^-$ ($v=0$), $N=0,1$, $B=0-10$ T.

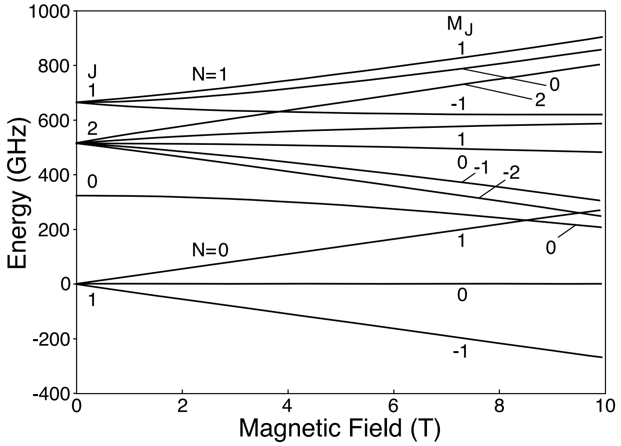

FIG. 5. Zeeman energies of SH^+, $X\,^3\Sigma^-$ ($v=0$), $N=0,1$, $B=0-10$ T.

Precision mass measurements have not yet been carried out with either of these ions. We note that FH^+ provides a convenient route to the mass of ^{19}F by comparison with ^{20}Ne or $^{12}CD_4{}^+$, both which are known to better than 100 ppt. It has also been proposed that $^{35}ClH^+$, compared with $^{36}Cl^+$, would enable a yet more precise intercomparison of mass and gamma-ray spectroscopy of neutron binding energies [12]. This is because ^{35}Cl has a particularly large neutron capture cross-section facilitating precision gamma-ray spectroscopy. Table VI shows a spectrum of polarizabilities that will lead to fractional cyclotron frequency shifts up to ±150 ppt, complicating obtaining a mass comparison at 10 ppt precision.

D. NH^+ and PH^+

NH^+ has a $^2\Pi_{1/2}$ ground electronic state intermediate between Hund's (a) and (b) schemes due to the relatively large

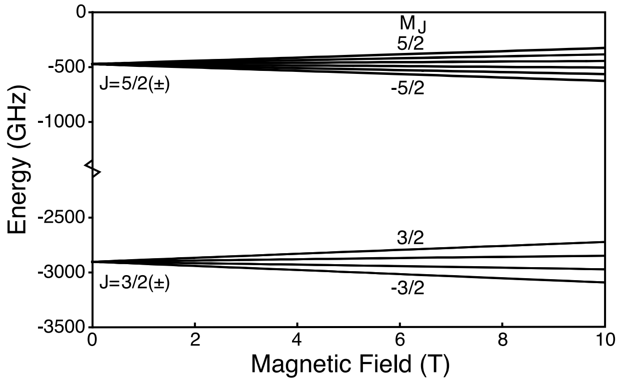

FIG. 6. Zeeman energies of FH^+, $X\,^2\Pi_{3/2}$ ($v=0$), $J=3/2$ and $5/2$, $B=0-10$ T.

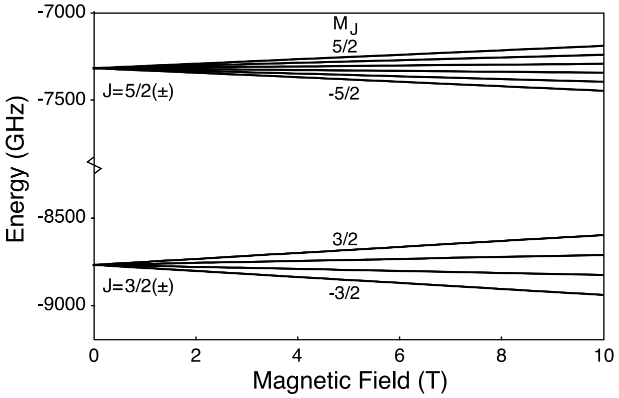

FIG. 7. Zeeman energies of ClH^+, $X\,^2\Pi_{3/2}$ $(v=0)$, $J=3/2$ and $5/2$, $B=0-10$ T.

rotational constant but small spin-orbit constant, see Table XIV. Unlike the other molecules with $^2\Pi$ states we found significant contributions from $\Delta\Omega=\pm1$ transitions and these were included in determining the polarizabilities. As Fig. 8 shows, the Zeeman effect in the $J=1/2$ level is nonlinear and small. This is because the contributions from the spin and orbital momentum cancel each other almost exactly. The polarizabilities in this level are very large, and are dominated by the contribution from the opposite parity lambda-doublet components, which are separated by only 7 GHz, see Table VII. The difference in the Zeeman splittings between the negative and positive parity state for this level arises because of the small, parity-dependent parameters g_l' and $g_r^{e\prime}$ in the Zeeman Hamiltonian. Because the Zeeman effect in this level is small the polarizabilities remain essentially constant over the field range. On the other hand, the $J=3/2$ level mixes with the $J=3/2$, $\Omega=3/2$ level which produces a small but significant Zeeman effect. The consequence is that the polarizabilities for the $J=3/2$ level are dependent on the field and decrease as the field increases.

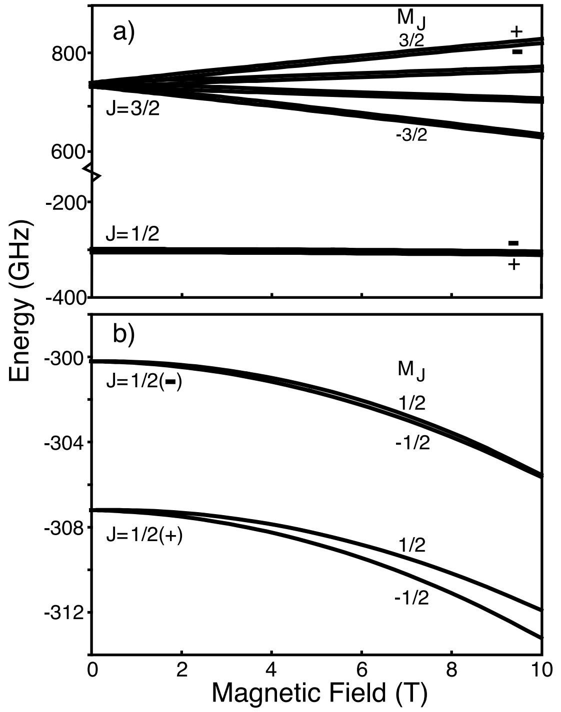

FIG. 8. Zeeman energies of NH^+, $X\,^2\Pi_{1/2}$ $(v=0)$, $B=0-10$ T: (a) $J=1/2$ and $3/2$, (b) expanded view of $J=1/2$.

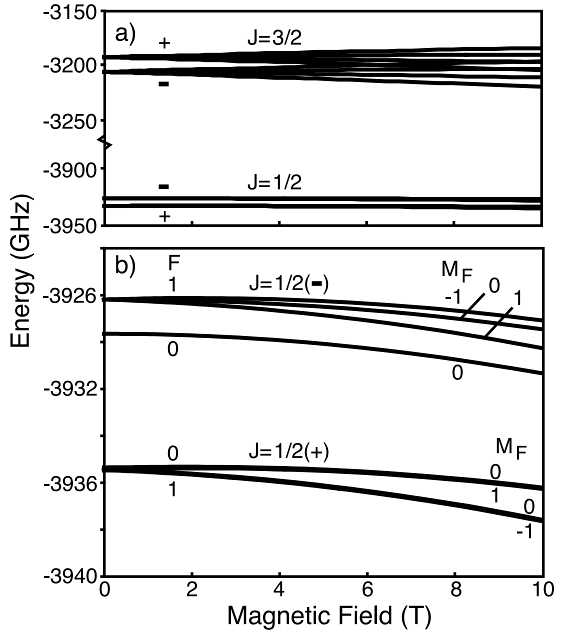

FIG. 9. Zeeman energies of PH^+, $X\,^2\Pi_{1/2}$ $(v=0)$, $B=0-10$ T: (a) $J=1/2$, $3/2$; (b) expanded view of $J=1/2$. F and M_F correspond to the hyperfine structure due to the nuclear spin of ^{31}P.

PH^+ also has a $^2\Pi_{1/2}$ ground electronic state, but is closer to Hund's case (a) and we are able to neglect contributions from $\Delta\Omega=\pm1$ transitions. Similar to NH^+ the $J=1/2$ level exhibits a small, nonlinear Zeeman effect, and large contributions to the polarizability from the opposite parity lambda-doubling components, see Fig. 9. PH^+ is the only species in this work that displays a significant hyperfine structure effect on the polarizability. This is because of the relatively large hyperfine interaction with the ^{31}P nucleus together with the small Zeeman effect in the $J=1/2$ level: at the fields of interest the coupling between the electronic angular momenta and the spin of the ^{31}P nucleus is still significant. (For the proton in PH^+, and for the other molecules with hyperfine structure, the Zeeman effect essentially decouples the nuclear spins from the rotational angular momentum, resulting in independent manifolds corresponding to the different nuclear spin projections M_I.) We therefore included the hyperfine interaction with the ^{31}P nucleus in the effective Hamiltonian (the relevant hyperfine parameters are included in Table XV), and so obtained polarizabilities for the hyperfine levels labelled with different M_I $(^{31}P)=\pm1/2$ (or in terms of M_F for the $J=1/2$ level). As Table VIII shows, the hyperfine dependence is quite significant for the $J=1/2$ level, but is smaller for $J=3/2$ where the Zeeman effect is larger.

As regards precision mass measurements, $^{14}NH^+$ and $^{15}NH^+$ provide another link between the mass of ^{14}N and ^{16}O, while $^{31}PH^+$ enables ^{31}P to be obtained from $^{16}O_2$. In addition, both ions, because they should exhibit a large "polarizability structure" in the lowest rotational level, are good candidates for testing our model and for measuring the ion dipole moments.

IV. CONCLUSIONS

Using calculated dipole moments and an effective Hamiltonian model we have obtained orientation polarizabilities, in high magnetic fields, of CO^+ and the open-shell diatomic hydride cations NH^+, OH^+, FH^+, PH^+, SH^+, ClH^+ in low-lying rotational levels. At the fields of interest, the polarizabilities of the remaining ions in the sequence LiH^+ to ArH^+, which have $^1\Sigma^+$ or $^2\Sigma^+$ ground states, can be obtained from a simple expression for closed-shell molecules. We expect the predicted polarizabilities to be accurate to better than ±2%, limited by uncertainty in the dipole moments; we expect errors due to the Born-Oppenheimer approximation and the effective Hamiltonian model to be smaller. These polarizabilities are hence useful for correcting a number of past and proposed precision mass comparisons, enabling mass comparison at the level of 10 ppt or better. In the case of CO^+, we confirm the polarizability calculation of Thompson *et al.* [1], and our theoretical dipole is in good agreement with their experimental result. However, without an independent check of the accuracy of our calculated dipole moment, our theoretical value for the polarizability correction does not enable an improved value for the $N_2{}^+/CO^+$ mass ratio. Except for favorable cases where the corrections are small, these uncertainties pose an obstacle to using mass comparisons with polar molecules to obtain atomic masses at the 1 ppt level. At this level of precision one must also consider including the distortion contribution to the polarizability.

On the other hand, using the effective Hamiltonian calculations of polarizability as the necessary link, precision cyclotron frequency measurements can be used to measure dipole moments of molecular ions. The experimental situation is most advantageous here for such cases as CO^+, or diatomics with $^2\Pi_{3/2}$ or $^2\Pi_{1/2}$ states, which show large shifts between different levels that are populated at 4.2 K. An extreme example is NH^+, which at 8.5 T, should exhibit very large polarizability shifts of $\pm 6\times 10^{-9}$ for the two lambda-doubling components of $J=1/2$, and for which a sub-1% measurement of the dipole seems feasible. We also note that polarizability shifts provide a nondestructive means of monitoring the rotational state of the ion. The example of $^{14}NH^+$ in fact has a total of 24 Zeeman-hyperfine-lambda-doubling sublevels associated with the $J=1/2$ ground rotational level. This structure could be accurately probed using single- and double-resonance RF spectroscopy with detection via a resulting shift in cyclotron frequency. This relatively rich structure, and the long coherence times associated with such isolated ions, may have application to experimental studies of quantum information.

ACKNOWLEDGMENTS

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APPENDIX: MOLECULAR PARAMETERS

This following tables (Tables IX–XV) give the molecular parameters used in the calculation of the polarizabilities of the open-shell molecular ions.

TABLE IX. Molecular parameters for CO^+, $X\ ^2\Sigma^+$, $v=0$.

Parameter [29]	Value/GHz
B_0	58.98303
D_0	0.18937×10^{-3}
γ_0	0.27297
g_S	2.0020
g_r	-0.306×10^{-3}
g_l	-0.231×10^{-2}

TABLE X. Molecular parameters for OH^+, $X\ ^3\Sigma^-$, $v=0$.

Parameter [34,63,64]	Value/GHz
B_0	492.345 93
D_0	0.057 505
H_0	3.6150×10^{-6}
γ_0	−4.533 69
λ_0	64.244 74
γ_D	7.91×10^{-4}
g_S	2.0020
g_r	-1.470×10^{-3}
g_l	4.408×10^{-3}

TABLE XI. Molecular parameters for SH^+, $X\ ^3\Sigma^-$, $v=0$.

Parameter [41]	Value/GHz
B_0	273.8084
D_0	0.014502
γ_0	−4.9727
λ_0	171.2355
g_S	2.0017
g_r	-0.63×10^{-3}
g_l	0.908×10^{-2}

TABLE XII. Molecular parameters for HF$^+$, $X\,^2\Pi$, $v=0$.

Parameter [35]	Value/GHz
B_0	513.2195
D_0	0.066806
H_0	4.905×10^{-6}
a_0	−8736.638
γ_0	−8.258
γ_D	0.240×10^{-2}
$p+2q$	15.4184
p_D+2q_D	-0.182×10^{-2}
q	−1.20060
q_D	0.34×10^{-3}
g_S	2.0020
g_L	1.00118
g_r	-0.57×10^{-3}
g_l^e	0.91×10^{-2}
$g_r^{e\prime}$	0.2339×10^{-2}
$g_l'-g_r^{e\prime}$	0.1502×10^{-1}

TABLE XIII. Molecular parameters of HCl$^+$, $X\,^2\Pi$, $v=0$.[a]

Parameter [42,65,66]	Value/GHz
B_0	293.47258
D_0	0.016421
H_0	4.569×10^{-7}
γ_0	−9.1297
A_0	−19279.4
A_D	0.06260
$p+2q$	17.5891
p_D+2q_D	-8.811×10^{-4}
q	−3.34796
q_D	4.704×10^{-5}
g_S	2.002
g_L	0.99937
g_r	-0.3083×10^{-3}
g_l^e	0.01555
$g_r^{e\prime}$	0.001142
$g_l'-g_r^{e\prime}$	0.02971

[a] The results of Saenger *et al.*[65] were refitted to take account of the different effective Hamiltonian used in that work from that used here.

TABLE XIV. Molecular parameters for NH$^+$, $X\,^2\Pi$, $v=0$.

Parameter [33]	Value/GHz
B_0	459.61565
D_0	0.0489051
H_0	0.3819×10^{-5}
A_0	2450.501153
γ_0	−2.4919
γ_D	0.4437×10^{-3}
$p+2q$	6.99416
p_D+2q_D	-0.9473×10^{-3}
q	1.65003
q_D	-0.2596×10^{-3}
g_S	2.002
g_L	1.0
g_r	-0.3046×10^{-2}
g_l^e	0.54×10^{-2}
$g_r^{e\prime}$	-0.3590×10^{-2}
$g_l'-g_r^{e\prime}$	0.7609×10^{-2}

TABLE XV. Molecular parameters for PH$^+$, $X\,^2\Pi$, $v=0$.

Parameter [40,67]	Value/GHz
B_0	251.429
D_0	0.01277
γ_0	−2.713
A_0	8875.06
$p+2q$	6.8802
q	0.3508
a	0.915
b	0.3857
$(b+c)$	−0.1863
d	1.184
g_S	2.0020
g_L	1.0
g_r	-0.1671×10^{-2}
g_l^e	0.5395×10^{-2}
$g_r^{e\prime}$	-0.1395×10^{-2}
$g_l'-g_r^{e\prime}$	0.1368×10^{-1}

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