

# Static and dynamic polarizability and the Stark and blackbody-radiation frequency shifts of the molecular hydrogen ions $\text{H}_2^+$ , $\text{HD}^+$ , and $\text{D}_2^+$

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We calculate the dc Stark effect for three molecular hydrogen ions in the nonrelativistic approximation. The effect is calculated both in dependence on the rovibrational state and in dependence on the hyperfine state. We discuss special cases and approximations. We also calculate the ac polarizabilities for several rovibrational levels and therefrom evaluate accurately the blackbody radiation shift, including the effects of excited electronic states. The results enable the detailed evaluation of certain systematic shifts of the transitions frequencies for the purpose of ultrahigh-precision optical, microwave, or radio-frequency spectroscopy in ion traps.

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## I. INTRODUCTION

The molecular hydrogen ions represent a family of simple quantum systems that are amenable both to high-precision ab initio calculations [1,2] and to high-precision spectroscopy. Therefore, they are of great interest for the determination of fundamental constants [3], for tests of the time- and gravitational-potential independence of fundamental constants [4,5], and for tests of QED [2]. On the experimental side, after early pioneering work on uncooled trapped ions and ions beams [6–8], the sympathetic cooling of trapped molecular hydrogen ions [9,10] has opened up the window for high-precision radio-frequency, rotational, and rovibrational spectroscopy. Precision infrared laser spectroscopy of two rovibrational transitions has been achieved [3,11], and the fundamental rotational transition has also been observed [12].

Because of the advances in experimental accuracy, and in order to open perspectives for future work directions, it has become important to evaluate the systematic effects on the transition frequencies. It is an advantage of the molecular hydrogen ion family that the sensitivities to external fields can be calculated ab initio. The systematic effects treated so far include the Zeeman shift [13–15], the electric quadrupole shift [16], and the blackbody radiation (BBR) shift [17]. The electric polarizability of the rovibrational levels of the molecular hydrogen ions has been of interest for a long time. It was computed with high accuracy for a subset of levels by several authors, in particular [18–23]. These calculations used adiabatic or nonadiabatic wave functions. Reference [20] reviews the experimental and theoretical values for the ground state of  $\text{H}_2^+$  and  $\text{D}_2^+$ . A particularly accurate calculation of the polarizability of  $\text{H}_2^+$  in its ground state was performed by one of the present authors, by including the relativistic corrections [24]. The dependence of the polarizability on the hyperfine state has only recently been obtained [25], for the

case of  $\text{HD}^+$ , and it was shown that the dependence is very significant. These results have permitted a first analysis of the potential for ultrahigh accuracy spectroscopy of  $\text{HD}^+$  and its suitability as an optical clock [16,26].

In the present paper, extensive calculations of the polarizability are presented. Its dependence on the hyperfine state is derived in a more elegant way and discussed in depth, both for  $\text{HD}^+$  and  $\text{H}_2^+$ , since it is of great relevance for experiments.

While the BBR shift is tiny, it will eventually become of relevance for experiments requiring the highest levels of accuracy, such as the mentioned test of time independence of fundamental constants. Therefore, this shift is also computed in detail. Results for  $\text{H}_2^+$  are presented for the first time. In addition, the case of  $\text{HD}^+$  is treated extensively, in view of the current experimental interest in this molecule.

This paper is structured as follows: In Sec. II we briefly review the calculation approach for the polarizability of the molecular hydrogen ions, neglecting spin effects. We define the effective Hamiltonian and present the tables of polarizabilities. In Sec. III we introduce the hyperfine structure (HFS) and discuss the computation of the dc Stark shift in dependence of the spin state. We also give a number of useful approximations. Section IV presents detailed results for a large number of hyperfine states potentially relevant for high-precision spectroscopy. In Sec. V we discuss the energy-level shifts induced by the oscillating (ac) electric field of the blackbody radiation, which we accurately evaluate by taking into account the precise frequency dependence of the polarizability.

## II. EVALUATION OF POLARIZABILITY

### A. Nonrelativistic polarizability: Spin-independent spatial considerations

For the purposes of evaluating the systematic effects in spectroscopy, it is at present sufficient to use the nonrelativistic

approximation to the polarizability. Therefore, we start from the nonrelativistic Schrödinger equation:

$$(H_0 - E)\Psi_0 = 0,$$

$$H_0 = -\frac{1}{2M_1}\nabla_1^2 - \frac{1}{2M_2}\nabla_2^2 - \frac{1}{2m_e}\nabla^2$$

$$+ \frac{1}{R} - \frac{1}{r_1} - \frac{1}{r_2}, \quad (1)$$

where  $M_1$  and  $M_2$  are the masses of the nuclei (proton or deuteron),  $R$  is the internuclear distance,  $r_1$  and  $r_2$  are the distances from nucleus 1 and 2 to the electron, respectively. The state  $\Psi_0 = |v L\rangle$  is the unperturbed state characterized by the vibrational and rotational quantum numbers  $v$ ,  $L$ , and  $E_0$  is its energy.

The interaction with an external electric field  $\mathbf{E}$  in the dipole interaction form is expressed by

$$V_p = -\mathbf{E} \cdot \mathbf{d}, \quad \mathbf{d} = e[Z(\mathbf{R}_1 + \mathbf{R}_2) - \mathbf{r}], \quad (2)$$

where  $\mathbf{d}$  is the electric dipole moment of the three-particle-system,  $\mathbf{R}_1$ ,  $\mathbf{R}_2$ , and  $\mathbf{r}$  are the position vectors of the nuclei and of the electron with respect to the center of mass.

Since the static or quasistatic electric fields present in an ion trap, and also the electric field of the radiation from continuous-wave lasers and from the blackbody environmental radiation, are typically weak, it is sufficient to apply second-order perturbation theory for the calculation of the polarizability. The energy shifts that result are typically at the level of 1 Hz, orders of magnitude smaller than the rotational or hyperfine splittings. For effects of higher order in the external electric field, see Ref. [19].

The change of energy due to the polarizability of a molecular ion is expressed by

$$E_p^{(2)} = \langle \Psi_0 | V_p (E_0 - H_0)^{-1} V_p | \Psi_0 \rangle$$

$$= E^i E^j \langle \Psi_0 | d^i (E_0 - H_0)^{-1} d^j | \Psi_0 \rangle$$

$$= -\frac{1}{2} \alpha_d^{ij} E^i E^j, \quad (3)$$

where  $\alpha_d^{ij}$ , the polarizability tensor of rank 2, has been introduced,

$$\alpha_d^{ij} = -2 \langle \Psi_0 | d^i (E_0 - H_0)^{-1} d^j | \Psi_0 \rangle. \quad (4)$$

The static dipole polarizability tensor is then reduced to scalar  $\alpha_s$  and tensor  $\alpha_t$  terms, which may be expressed in terms of three contributions corresponding to the possible values of the rotational angular momentum quantum number of the intermediate state;  $L' = L \pm 1$ , or  $L' = L$ :

$$a_+ = \frac{2}{2L+1} \sum_p \frac{\langle vL \|\mathbf{d}\| p(L+1) \rangle \langle p(L+1) \|\mathbf{d}\| vL \rangle}{E_0 - E_p},$$

$$a_0 = -\frac{2}{2L+1} \sum_p \frac{\langle vL \|\mathbf{d}\| pL \rangle \langle pL \|\mathbf{d}\| vL \rangle}{E_0 - E_p}, \quad (5)$$

$$a_- = \frac{2}{2L+1} \sum_p \frac{\langle vL \|\mathbf{d}\| p(L-1) \rangle \langle p(L-1) \|\mathbf{d}\| vL \rangle}{E_0 - E_p},$$

where  $L$  is the rotational quantum number of the state under consideration,  $E_0$  is its energy, and  $E_p$  is the nonrelativistic energy of the intermediate state  $|p L'\rangle$ .

The polarizability tensor may be expressed as

$$\alpha_d^{ij} = \delta_{ij} \alpha_s + \alpha_t \langle \Psi_0 | L_i L_j + L_j L_i - \frac{2}{3} \delta_{ij} \mathbf{L}^2 | \Psi_0 \rangle, \quad (6)$$

where  $L_i$  are the Cartesian components of the rotational angular momentum operator,  $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$ , and

$$\alpha_s = \frac{1}{3}(a_+ + a_0 + a_-),$$

$$\alpha_t = -\frac{a_+}{2(L+1)(2L+3)} + \frac{a_0}{2L(L+1)} - \frac{a_-}{2L(2L-1)}.$$

We may also define longitudinal ( $\alpha_{\parallel}$ ) and transverse ( $\alpha_{\perp}$ ) polarizabilities

$$\alpha_{\parallel} = \alpha_s + \alpha_t \langle \Psi_0 | 2L_z^2 - \frac{2}{3} \mathbf{L}^2 | \Psi_0 \rangle, \quad (7)$$

$$\alpha_{\perp} = \frac{1}{2}(\alpha_d^{xx} + \alpha_d^{yy}) = \alpha_s + \alpha_t \langle \Psi_0 | L_x^2 + L_y^2 - \frac{2}{3} \mathbf{L}^2 | \Psi_0 \rangle$$

$$= \alpha_s - \frac{1}{2} \alpha_t \langle \Psi_0 | 2L_z^2 - \frac{2}{3} \mathbf{L}^2 | \Psi_0 \rangle. \quad (8)$$

The definition of  $\alpha_{\perp}$  as given above is reasonable, since axial symmetry requires that the matrix elements of  $L_x^2$  and of  $L_y^2$  are equal. Thus, the polarizabilities  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  actually involve the expectation value of only a single operator, which has an alternative representation as the zero component of the rank-two tensor  $\{\mathbf{L} \otimes \mathbf{L}\}_2$ ,

$$2L_z^2 - \frac{2}{3} \mathbf{L}^2 = \sqrt{\frac{8}{3}} \{\mathbf{L} \otimes \mathbf{L}\}_{20}. \quad (9)$$

In Sec. III, we will evaluate the polarizabilities of the hyperfine states of a given rovibrational level. The approximation we will use consists in introducing the polarizability operator, which acts in a manifold of given  $L$ ,

$$\hat{\alpha}_d^{ij}(v, L) = \delta_{ij} \alpha_s(v, L) + \alpha_t(v, L) \left[ L_i L_j + L_j L_i - \frac{2}{3} \delta_{ij} \mathbf{L}^2 \right].$$

The operator  $\hat{\alpha}_d$  is the sum of a scalar and an irreducible tensor of rank 2; in what follows we use instead the following linear combinations:

$$\hat{\alpha}_{\parallel}(v, L) = \alpha_s(v, L) + \alpha_t(v, L) \sqrt{\frac{8}{3}} \{\mathbf{L} \otimes \mathbf{L}\}_{20},$$

$$\hat{\alpha}_{\perp}(v, L) = \alpha_s(v, L) - \frac{1}{2} \alpha_t(v, L) \sqrt{\frac{8}{3}} \{\mathbf{L} \otimes \mathbf{L}\}_{20},$$

which are defined in such a way that their expectation values give the Stark shift in an electric field along or orthogonal to the quantization axis, respectively. Here, we have included the explicit dependence of the coefficients  $\alpha_s$ ,  $\alpha_t$  on the vibrational and rotational quantum numbers  $v$ ,  $L$ . We shall also explicitly consider the polarizability anisotropy operator,

$$\hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} = \alpha_t(v, L) \frac{3}{2} \sqrt{\frac{8}{3}} \{\mathbf{L} \otimes \mathbf{L}\}_{20} = 3\alpha_t(v, L) \left( L_z^2 - \frac{1}{3} \mathbf{L}^2 \right). \quad (10)$$

## B. Numerical results

Wave functions of the rovibrational states in the molecular hydrogen ions are obtained by using the variational approach expounded in Ref. [24]. Briefly, the wave function for a state with a total orbital angular momentum  $L$  and of a total spatial

TABLE I. Polarizabilities of the HD<sup>+</sup> molecular ion in atomic units.

$v$	$L = 0$		$L = 1$		$L = 2$		$L = 3$		$L = 4$		$L = 5$	
	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$
0	395.30633	3.99015	175.48275	4.00956	13.82797	4.03878	3.19075	4.07794	1.10141	4.12721	0.47319	
1	462.65271	4.70314	205.20067	4.72694	16.14340	4.76278	3.71557	4.81084	1.27799	4.87136	0.54642	
2	540.68636	5.56925	239.58035	5.59871	18.81611	5.64313	4.31921	5.70273	1.48001	5.77786	0.62955	
3	631.40288	6.63284	279.47585	6.66965	21.91000	6.72541	5.01516	6.80017	1.71152	6.89451	0.72396	
4	737.31802	7.95478	325.95893	8.00132	25.50477	8.07195	5.82011	8.16691	1.97742	8.28690	0.83127	
5	861.64968	9.61839	380.39514	9.67856	29.70139	9.76943	6.75494	9.89175	2.28374	10.04654	0.95337	
6	1008.5802	11.74323	444.54814	11.82178	34.62944	11.94052	7.84610	12.10056	2.63789	12.30342	1.09241	
7	1183.6432	14.50032	520.73882	14.60466	40.45801	14.76254	9.12757	14.97563	3.04910	15.24624	1.25088	
8	1394.3075	18.14238	612.07821	18.28368	47.41173	18.49776	10.64364	18.78717	3.52889	19.15548	1.43147	
9	1650.8846	23.05215	722.82833	23.24788	55.79504	23.54473	12.45301	23.94684	4.09171	24.45984	1.63690	
10	1967.9875	29.82774	858.97404	30.10584	66.03006	30.52844	14.63477	31.10210	4.75562	31.83608	1.86935	

parity  $\pi = (-1)^L$  is expanded as follows:

$$\Psi_{LM}^\pi(\mathbf{R}, \mathbf{r}_1) = \sum_{l_1+l_2=L} \mathcal{Y}_{LM}^{l_1 l_2}(\hat{\mathbf{R}}, \hat{\mathbf{r}}_1) G_{l_1 l_2}^{L\pi}(R, r_1, r_2),$$

$$G_{l_1 l_2}^{L\pi}(R, r_1, r_2) = \sum_{n=1}^N \{C_n \text{Re}[e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2}] + D_n \text{Im}[e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2}]\}, \quad (11)$$

where the complex exponents  $\alpha$ ,  $\beta$ ,  $\gamma$ , are generated in a pseudorandom way. The use of complex exponents instead of real ones allows reproducing the oscillatory behavior of the vibrational part of the wave function and improves the convergence rate. In numerical calculations we utilize basis sets as large as  $N = 7000$  functions in order to provide the required accuracy for the static polarizability of about eight significant digits.

We note that a variational principle holds for the numerical value for  $\alpha_s$  (but not for  $\alpha_t$ ): the larger the value, the closer it is to the exact (nonrelativistic) value, provided that the initial wave function is accurate enough.

The results of numerical calculations of the polarizabilities for a wide range of rovibrational states are presented in

Tables I–III. These polarizabilities do not include relativistic corrections. These have so far been computed only for the ground rovibrational level ( $v = 0, L = 0$ ) of  $\text{H}_2^+$  [24]. Therefore, the relative inaccuracy of the values of the table as compared to the exact values is of order  $\alpha^{-2} \simeq 1 \times 10^{-4}$ . This is sufficiently small for current and near-future purposes.

### C. Scaling with rotational angular momentum

For large  $L$ , we find for  $\text{HD}^+$ ,

$$\alpha_t(v, L) \propto \frac{1}{L(L+1)(2L-1)(2L+3)}. \quad (12)$$

This follows from an argument described below after Eq. (25).

We found heuristically that, for  $\text{H}_2^+$  and  $\text{D}_2^+$ ,

$$\alpha_t(v, L) \propto \frac{1}{(2L-1)(2L+3)}. \quad (13)$$

### D. Comparison with previous work

#### 1. Contribution from ground electronic state

An approximation to the polarizability can be obtained using the well-known sum-over-intermediate-states expression,

TABLE II. Polarizabilities of the  $\text{H}_2^+$  molecular ion in atomic units.

$v$	$L = 0$		$L = 1$		$L = 2$		$L = 3$		$L = 4$		$L = 5$	
	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$
0	3.1687258	3.1783035	-0.8033729	3.1975081	-0.1931423	3.2264392	-0.0914467	3.2652493	-0.0544769	3.3141473	-0.0367142	
1	3.8975634	3.9101018	-1.1442051	3.9352574	-0.2751013	3.9731892	-0.1302653	4.0241411	-0.0776138	4.0884471	-0.0523179	
2	4.8215004	4.8380889	-1.6000689	4.8713900	-0.3847653	4.9216560	-0.1822373	4.9892726	-0.1086157	5.0747693	-0.0732474	
3	6.0093275	6.0315483	-2.2129563	6.0761862	-0.5322759	6.1436389	-0.2521973	6.2345166	-0.1503892	6.3496578	-0.1014845	
4	7.5604532	7.5906530	-3.0434869	7.6513642	-0.7322875	7.7432180	-0.3471422	7.8671844	-0.2071498	8.0246002	-0.1399110	
5	9.6217735	9.6635170	-4.1811566	9.7475033	-1.0064626	9.8747452	-0.4774336	10.046804	-0.2851555	10.265837	-0.1928182	
6	12.416000	12.474853	-5.7615823	12.593371	-1.3876723	12.773211	-0.6588274	13.016932	-0.3939491	13.328069	-0.2667729	
7	16.290999	16.375936	-7.9965515	16.547168	-1.9273337	16.807463	-0.9160304	17.161118	-0.5485440	17.614095	-0.3721509	
8	21.809473	21.935532	-11.228720	22.189990	-2.7087984	22.577626	-1.2892120	23.105870	-0.7734466	23.785138	-0.5259729	
9	29.920328	30.113886	-16.036300	30.505195	-3.8730473	31.102847	-1.8465559	31.920266	-1.1104555	32.976407	-0.7574477	
10	42.306330	42.616316	-23.445884	43.244200	-5.6711124	44.206257	-2.7100058	45.528094	-1.6347702	47.246181	-1.1195247	

TABLE III. Polarizabilities of the  $D_2^+$  molecular ion in atomic units.

$v$	$L = 0$		$L = 1$		$L = 2$		$L = 3$		$L = 4$		$L = 5$	
	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$	$\alpha_s$	$\alpha_t$
0	3.0719887	3.0765904	-0.7579521	3.0858052	-0.1813435	3.0996560	-0.0852443	3.1181777	-0.0503016	3.1414173	-0.0335048	
1	3.5530258	3.5585822	-0.9782731	3.5697111	-0.2340592	3.5864444	-0.1100266	3.6088309	-0.0649271	3.6369364	-0.0432481	
2	4.1195817	4.1263238	-1.2485988	4.1398301	-0.2987476	4.1601453	-0.1404432	4.1873367	-0.0828824	4.2214959	-0.0552137	
3	4.7912827	4.7995087	-1.5808716	4.8159913	-0.3782716	4.8407920	-0.1778439	4.8740043	-0.1049671	4.9157545	-0.0699367	
4	5.5933149	5.6034134	-1.9904009	5.6236531	-0.4763025	5.6541185	-0.2239603	5.6949390	-0.1322078	5.7462891	-0.0881048	
5	6.5583187	6.5708021	-2.4970077	6.5958274	-0.5975951	6.6335113	-0.2810366	6.6840342	-0.1659357	6.7476365	-0.1106108	
6	7.7290547	7.7446049	-3.1266348	7.7757864	-0.7483752	7.8227607	-0.3520126	7.8857801	-0.2078964	7.9651778	-0.1386263	
7	9.1622096	9.1817469	-3.9136471	9.2209342	-0.9368936	9.2799934	-0.4407873	9.3592871	-0.2604068	9.4592730	-0.1737083	
8	10.933925	10.958708	-4.9041723	11.008431	-1.1742306	11.083398	-0.5526002	11.184144	-0.3265836	11.311297	-0.2179539	
9	13.147977	13.179752	-6.1610454	13.243527	-1.4754879	13.339760	-0.6946003	13.469145	-0.4106838	13.632624	-0.2742310	
10	15.948121	15.989359	-7.7712809	16.072159	-1.8615919	16.197178	-0.8766990	16.365416	-0.5186172	16.578236	-0.3465280	

where the sum is truncated to a subset of levels. For  $HD^+$ , such a calculation has been performed using transition dipole moments computed in the Born-Oppenheimer approximation [25], including in the sum only levels of the ground electronic state (the inaccuracy of the used dipole moments is mentioned further below). At first sight, it may appear that the polarizability of a level  $(v, L)$  in  $HD^+$  is dominated by the contribution from the rotational levels adjacent in energy to the particular state, namely  $(v, L \pm 1)$ . This is evidently true for  $L = 0$  levels. However, for  $L \neq 0$ , there is partial cancellation of the two contributions from  $L' = L \pm 1$ . Even then, the  $\alpha_t$  values indeed arise essentially from the rovibrational transitions. However, the  $\alpha_s(L > 0)$  values are actually dominated by the contribution from the excited electronic states. This has been pointed out by several authors before. The comparison of the accurate results given in the tables above with the truncated-sum results allows us to put in evidence the contribution from the excited electronic states. The comparison is shown in Table IV, showing that for low-lying rovibrational levels  $(v, L < 5)$ , the difference is of order several atomic units for  $\alpha_s$  and less than 2.5 atomic units for  $\alpha_t$ . The increase of the difference with  $v$  is due to the fact that the contributions from excited electronic states become more important since the level

TABLE IV. Difference  $\delta\alpha$  between the accurate polarizabilities of  $HD^+$  (this work) and those computed by a summation over all intermediate rovibrational states in the ground electronic state, in atomic units. The latter are calculated from the results of Ref. [25] (which are there given in terms of  $\alpha_{vLFSJJ_z}^{(l)}, \alpha_{vLFSJJ_z}^{(r)}$ ) as  $\alpha_s(v, L) = (\alpha_{vLFSJJ_z}^{(l)} + 2\alpha_{vLFSJJ_z}^{(r)})/3$  [where any hyperfine state  $(F, S, J, J_z)$  can be chosen] and  $\alpha_t(v, L) = (\alpha_{vLn_s}^{(l)} - \alpha_{vLn_s}^{(r)})/[L(2L - 1)]$ , where  $n_s$  denotes the stretched state, defined in Sec. III C 3.

$v$	$L = 0$		$L = 1$		$L = 2$		$L = 3$		$L = 4$	
	$\delta\alpha_s$	$\delta\alpha_t$	$\delta\alpha_s$	$\delta\alpha_t$	$\delta\alpha_s$	$\delta\alpha_t$	$\delta\alpha_s$	$\delta\alpha_t$	$\delta\alpha_s$	$\delta\alpha_t$
0	3.3	3.1	-0.72	3.1	-0.18	3.2	-0.08	3.2	-0.06	
1	3.9	3.7	-0.98	3.8	-0.24	3.8	-0.12	3.8	-0.08	
2	4.7	4.5	-1.34	4.5	-0.34	4.6	-0.16	4.6	-0.10	
3	5.6	5.4	-1.80	5.5	-0.44	5.5	-0.22	5.6	-0.12	
4	6.8	6.6	-2.42	6.6	-0.60	6.7	-0.28	6.8	-0.16	

$v$  is getting closer in energy to them. Note that the values in Table IV are similar to those in Tables II, III, as it should be, according to the above interpretation.

For the homonuclear  $H_2^+$  and  $D_2^+$  the polarizability arises only from the excited electronic states, since there is no electric-dipole coupling between levels of the ground electronic state. As a consequence, the polarizabilities  $\alpha_s(L = 0)$  and  $\alpha_t(v, L)$  are much smaller than in the case of the heteronuclear ions, as has been noted in previous studies cited above.

## 2. General calculations

We can compare our results with some previous studies.

Early on, Bishop and Lam [18] studied the states  $v = 0, L = 0-10$  of  $H_2^+$ . The largest number of levels was considered by Moss and Valenzano, who covered the three ion species also treated here, with  $L = 0, 1$ , and all  $v$  [21]. Our results agree with theirs to within two units of the last digit reported by them, except for the level  $(v = 8, L = 1)$ , where the largest discrepancy occurs, 0.007 a.u.

The agreement with the  $L = 0$  values for the three ion species determined by Hilico *et al.* [20] and Karr *et al.* [23] is better than  $4 \times 10^{-8}$  in relative terms.

Pilon and Baye recently computed the polarizabilities of  $H_2^+$  for a number of levels [27]. The values for  $v = 0, L = 0, 1, 2, 3, 4, 5$  agree to better than  $2 \times 10^{-8}$  in relative terms. For  $L = 1, v = 0, 1, 2, 3$  and for  $L = 2, v = 0, 1, 2, 3$  the values agree with the present values to better than  $3 \times 10^{-7}$  in relative terms.

## III. PERTURBATION THEORY FOR HYPERFINE STATES

### A. Energy shifts

The hyperfine interactions split each rovibrational level into a number of hyperfine sublevels. We denote the corresponding kets as  $|m\rangle = |vLnJ_z\rangle$ , where  $n$  is a label for the particular hyperfine state in a rovibrational level  $(v, L)$  (note that this notation includes both pure and nonpure spin states).  $n$  is written as  $(F, S, J)$  for  $HD^+$  and  $(I, S, J)$  for  $H_2^+$ ; see Sec. III B below. When the Stark shifts of the quantum levels are small compared to other shifts, we can apply first-order perturbation theory. The Stark energy shift of a state  $|m\rangle$  can be expressed

in different ways [28]:

$$\begin{aligned}
 \Delta E(m) &= -\frac{1}{2}[\langle m|\hat{\alpha}_{\parallel}|m\rangle E_z^2 + \langle m|\hat{\alpha}_{\perp}|m\rangle(E_x^2 + E_y^2)] \\
 &= -\frac{1}{2}\left\{\alpha_s(E_x^2 + E_y^2 + E_z^2) + \alpha_t\left[E_z^2 - \frac{1}{2}(E_x^2 + E_y^2)\right]\langle m|\sqrt{\frac{8}{3}}\{\mathbf{L} \otimes \mathbf{L}\}_{20}|m\rangle\right\} \\
 &= -\frac{1}{2}\mathbf{E}^2\left[\alpha_s + \alpha_t(3\cos^2\theta - 1)\langle m|L_z^2 - \frac{1}{3}\mathbf{L}^2|m\rangle\right] \\
 &= -\frac{1}{2}\mathbf{E}^2\left[\alpha_s(v, L) + (3\cos^2\theta - 1)\frac{1}{3}\langle vLnJ_z|\hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp}|vLnJ_z\rangle\right], \tag{14}
 \end{aligned}$$

where  $\theta$  is the angle between the quantization axis and the direction of the electric field  $\mathbf{E}$ .

In Refs. [16,25] the levels shifts were described in terms of longitudinal polarizability  $\alpha^{(l)}$  and transverse polarizability  $\alpha^{(t)}$ . They are related to the expectation values of the operators introduced here by  $\langle m|\hat{\alpha}_{\parallel}|m\rangle = \alpha^{(l)}$  and  $\langle m|\hat{\alpha}_{\perp}|m\rangle = \alpha^{(t)}$ .

### B. Hyperfine structure

We limit ourselves in the following to the ion species  $\text{H}_2^+$  and  $\text{HD}^+$ , which are most relevant for experimental work at present.

In case of the molecular ion  $\text{H}_2^+$  we have identical nuclei and nuclear permutation symmetry. This makes some spin configurations forbidden and splits the consideration of hyperfine states into two cases (see Ref. [29]): for even  $L$ , the total nuclear spin  $I$  is zero and only two hyperfine sublevels are possible; for states with odd  $L$ , the total nuclear spin is one and the rovibrational level is split into five or six hyperfine sublevels, depending on the value of  $L$ .

The most suitable coupling scheme of the angular momentum operators is

$$\mathbf{S} = \mathbf{I} + \mathbf{s}_e, \quad \mathbf{J} = \mathbf{S} + \mathbf{L}, \tag{15}$$

where  $\mathbf{I}$  is the total nuclear spin operator, and  $\mathbf{s}_e$  is the electron spin operator. The basis states which correspond to this coupling are

$$|ISLJJ_z\rangle = \sum_{I_z, \xi, S_z} C_{SS_z, LL_z}^{JJ_z} C_{II_z, s_e \xi}^{SS_z} (|II_z\rangle \cdot |s_e \xi\rangle \cdot |LL_z\rangle), \tag{16}$$

and will be called pure states [30].

The effective HFS Hamiltonian is expressed as [29]

$$\begin{aligned}
 H_{\text{eff}} &= b_F(\mathbf{I} \cdot \mathbf{s}_e) + c_e(\mathbf{L} \cdot \mathbf{s}_e) + c_I(\mathbf{L} \cdot \mathbf{I}) \\
 &+ \frac{d_1}{(2L-1)(2L+3)} \left\{ \frac{2}{3}\mathbf{L}^2(\mathbf{I} \cdot \mathbf{s}_e) - [(\mathbf{L} \cdot \mathbf{I})(\mathbf{L} \cdot \mathbf{s}_e) \right. \\
 &+ (\mathbf{L} \cdot \mathbf{s}_e)(\mathbf{L} \cdot \mathbf{I}) \left. \right\} + \frac{d_2}{(2L-1)(2L+3)} \\
 &\times \left[ \frac{1}{3}\mathbf{L}^2\mathbf{I}^2 - \frac{1}{2}(\mathbf{L} \cdot \mathbf{I}) - (\mathbf{L} \cdot \mathbf{I})^2 \right]. \tag{17}
 \end{aligned}$$

For the case of even  $L$ , the pure states are the true HFS eigenstates, since the  $2 \times 2$  effective HFS Hamiltonian matrix is diagonal. Even for odd- $L$  states, the pure states are good approximations to the true HFS states [30], since the

coefficients of admixture of other states to a given true HFS state are small, e.g., for  $L = 1$  do not exceed 0.04, and for  $L = 3$  do not exceed 0.06. This means that even in this case, a good approximation for expectation values such as Eq. (14) may be obtained using the pure states.

For the hydrogen molecular ion  $\text{HD}^+$  the coupling scheme of the particle angular momentum operators is [31]

$$\mathbf{F} = \mathbf{I}_p + \mathbf{s}_e, \quad \mathbf{S} = \mathbf{F} + \mathbf{I}_d, \quad \mathbf{J} = \mathbf{S} + \mathbf{L}, \tag{18}$$

where  $\mathbf{I}_p, \mathbf{I}_d$  are the proton and deuteron spin operators, respectively. The effective Hamiltonian is given in Ref. [31]. The pure states are determined in a similar way as in Eq. (16). In zero magnetic field, the pure states represent a good approximation to some of the true HFS states and may be used to calculate approximate values of the polarizabilities. Details are given in Sec. IV below. Hyperfine states are labeled by  $n = (FSJ)$ .

### C. Analytical results

In this section we discuss some useful results that allow to understand several dependencies. In particular we discuss the polarizabilities of the pure spin states, for two reasons. First, a significant part of hyperfine states may be well approximated by pure spin states; second, since all hyperfine states can be expressed as weighted sums of pure spin states, their polarizabilities can conveniently be computed from the pure-state polarizabilities.

#### 1. Zero magnetic field

When the magnetic field is zero, the total angular momentum squared  $\mathbf{J}^2$  commutes with the hyperfine Hamiltonian and  $J$  is a good quantum number. Therefore we can apply the Wigner-Eckart theorem, and separate the  $J_z$  dependence of the expectation value:

$$\begin{aligned}
 &\langle vLnJ_z|\{\mathbf{L} \otimes \mathbf{L}\}_{20}|vLnJ_z\rangle \\
 &= C_{20, JJ_z}^{JJ_z} \langle vLn||\{\mathbf{L} \otimes \mathbf{L}\}_2||vLn\rangle / \sqrt{2J+1} \\
 &= -\frac{J(J+1) - 3J_z^2}{\sqrt{J(J+1)(2J-1)(2J+1)(2J+3)}} \\
 &\times \langle vLn||\{\mathbf{L} \otimes \mathbf{L}\}_2||vLn\rangle. \tag{19}
 \end{aligned}$$

We therefore obtain the  $J_z$  dependence of the polarizability anisotropy as follows:

$$\begin{aligned} & \langle vLnJ_z | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | vLnJ_z \rangle \\ &= \frac{3J_z^2 - J(J+1)}{J(2J-1)} \langle vLnJ_z = J | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | vLnJ_z = J \rangle. \end{aligned} \quad (20)$$

Note that this result holds both for pure and nonpure spin states. It follows that for  $J = 0$  states, the polarizability anisotropy

is zero. For  $\text{HD}^+$ ,  $J = 0$  states can only occur for  $L < 3$ , since the minimum  $J$  value permitted by angular momentum algebra is  $L - 2$ . For  $\text{H}_2^+$ , there are no such states, since  $J$  is a half-integer number.

## 2. Pure states

For pure angular-momentum states, the matrix elements of the polarizability anisotropy can be evaluated explicitly. Considering only the coupling scheme  $\mathbf{J} = \mathbf{S} + \mathbf{L}$ , we have (note that this is independent of  $I$  or  $F$ )

$$\begin{aligned} \langle SLJJ_z | 2 \left( L_z^2 - \frac{1}{3} \mathbf{L}^2 \right) | SLJJ_z \rangle &= \sqrt{\frac{8}{3}} \langle SLJJ_z | \{ \mathbf{L} \otimes \mathbf{L} \}_{20} | SLJJ_z \rangle = \sqrt{\frac{8}{3}} \frac{C_{JJ_z, 20}^{JJ_z}}{\sqrt{2J+1}} \langle SLJ \| \{ \mathbf{L} \otimes \mathbf{L} \}_2 \| SLJ \rangle \\ &= -\frac{[J(J+1) - 3J_z^2][3D(D-1) - 4J(J+1)L(L+1)]}{3J(J+1)(2J-1)(2J+3)}, \end{aligned} \quad (21)$$

where

$$D = J(J+1) + L(L+1) - S(S+1). \quad (22)$$

This result is obtained using the following relations [32,33]:

$$\begin{aligned} \langle SLJ \| \{ \mathbf{L} \otimes \mathbf{L} \}_2 \| SLJ \rangle &= (2J+1)(-1)^{S+L+J+2} \begin{Bmatrix} L & L & 2 \\ J & J & S \end{Bmatrix} \langle L \| \{ \mathbf{L} \otimes \mathbf{L} \}_2 \| L \rangle, \\ \langle L \| \{ \mathbf{L} \otimes \mathbf{L} \}_2 \| L \rangle &= \frac{1}{\sqrt{6}} \sqrt{L(L+1)} \sqrt{(2L-1)(2L+1)(2L+3)}. \end{aligned}$$

In  $\text{H}_2^+$  we consider first the states having even  $L$ , so  $I = 0$ . Then  $S = 1/2$ . These pure states are exact HFS eigenstates, and therefore Eq. (22) immediately gives the exact Stark shift using Eqs. (14) and (20):

$$\langle m(\text{even } L) | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | m(\text{even } L) \rangle_{\text{H}_2^+} = -\frac{3}{2} \alpha_t(v, L) \frac{[J(J+1) - 3J_z^2][3D(D-1) - 4J(J+1)L(L+1)]}{3J(J+1)(2J-1)(2J+3)}, \quad (23)$$

with  $D = J(J+1) + L(L+1) - 3/4$ .

For pure states with odd  $L$  (and therefore  $I = 1$ ):

$$\begin{aligned} \langle I = 1SLJ \| \{ \mathbf{L} \otimes \mathbf{L} \}_2 \| I = 1SLJ \rangle &= (2J+1)(-1)^{S+L+J} \begin{Bmatrix} L & L & 2 \\ J & J & S \end{Bmatrix} \langle L \| \{ \mathbf{L} \otimes \mathbf{L} \}_2 \| L \rangle \\ &= \sqrt{\frac{2J+1}{6}} \frac{3D(D-1) - 4J(J+1)L(L+1)}{2\sqrt{J(J+1)(2J-1)(2J+3)}}, \end{aligned} \quad (24)$$

where  $D$  is given by Eq. (22). We see that the actual value of  $I$  does not occur on the right-hand side, and that we obtain the same result as for the  $I = 0$  pure states. Equation (23) is an approximate result also for the odd- $L$  hyperfine states of  $\text{H}_2^+$  which are not pure, provided they are approximately pure (see below).

In the case of  $\text{HD}^+$ , where the pure states are denoted as  $|FSLJJ_z\rangle$ , Eq. (23) also holds, where  $L$  now can be even or odd. There is no dependence on  $F$ .

Summarizing, for any pure state of  $\text{H}_2^+$  and  $\text{HD}^+$  and, by consequence, also for all other molecular hydrogen ions, Eq. (23) gives the polarizability anisotropy [with  $D$  given in Eq. (22)]

$$\langle \text{pure state} | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | \text{pure state} \rangle_{\text{any species}} = -\frac{3}{2} \alpha_t(v, L) \frac{[J(J+1) - 3J_z^2][3D(D-1) - 4J(J+1)L(L+1)]}{3J(J+1)(2J-1)(2J+3)}. \quad (25)$$

We note that Roeggen [34] developed an approximate theory of the polarizability of heteronuclear diatomic molecules with spin, neglecting nuclear spin. If we combine our Eq. (25) and the approximate dependencies Eq. (12) we reproduce the result given in Eqs. (62) and (63) of Ref. [34].

## 3. Stretched states

The stretched states are those exact HFS states having maximal total angular momentum  $J$  and maximal (absolute) projection  $|J_z|$ . These are also pure states. In  $\text{HD}^+$ , these are the states  $|vLn_s\rangle$ , where  $n_s$  denotes the stretched hyperfine

TABLE V. The normalized anisotropic polarizabilities for the  $J_z = 0$  hyperfine states of  $\text{HD}^+$  in  $L = 1$  levels. The first column shows the hyperfine state's label  $n, J_z$  ( $F$  and  $S$  are usually approximate,  $J$  is an exact quantum number), the second column contains the normalized values  $\langle vLFSJJ_z = 0 | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | vLFSJJ_z = 0 \rangle / \langle vLn_s | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | vLn_s \rangle$  for the pure state  $|vLFSJJ_z = 0\rangle$  giving the largest contribution to the exact HFS state  $|vLnJ_z = 0\rangle$  (note that the values are independent of  $F$  and of  $v$ ). The following columns give the actual values  $\langle vLnJ_z = 0 | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | vLnJ_z = 0 \rangle / \langle vLn_s | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | vLn_s \rangle$  for each hyperfine state. The normalization is with respect to the polarizability anisotropy of the stretched state  $|vLn_s\rangle$  of the same rovibrational level, Eq. (26). The three states marked with an asterisk are pure states. The values for states with  $J_z \neq 0$  are obtained by multiplying the values in the table by  $(1 - 3J_z^2/[J(J+1)])$ .

Hyp. state ( $F, S, J, J_z$ )	Eq. (25) (normalized)	Level				
		( $v, L$ ) = (0, 1)	( $v, L$ ) = (1, 1)	( $v, L$ ) = (2, 1)	( $v, L$ ) = (3, 1)	( $v, L$ ) = (4, 1)
(0, 1, 2, 0)	-1	-0.999422	-0.999457	-0.999491	-0.999525	-0.999558
(0, 1, 1, 0)	1	0.998747	0.998825	0.998902	0.998978	0.999053
(0, 1, 0, 0)*	0	0	0	0	0	0
(1, 0, 1, 0)	-2	-1.66845	-1.69239	-1.71585	-1.73892	-1.76151
(1, 1, 1, 0)	1	0.590503	0.619326	0.647628	0.675521	0.702883
(1, 1, 0, 0)*	0	0	0	0	0	0
(1, 1, 2, 0)	-1	-0.999973	-0.999972	-0.999971	-0.99997	-0.99997
(1, 2, 1, 0)	-0.2	-0.120803	-0.125763	-0.130681	-0.135574	-0.140428
(1, 2, 3, 0)*	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8
(1, 2, 2, 0)	1	0.999395	0.999429	0.999462	0.999495	0.999528

state:  $F = 1, S = 2, J = L + 2, J_z = \pm(L + 2)$ . We find from Eq. (25) or by analytical evaluation of the matrix elements for these two stretched states (the evaluation is simple, if the calculations is done with the basis functions being the eigenfunctions of the individual angular momenta  $I_p, I_d, S, L$ ),

$$\langle vLn_s | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | vLn_s \rangle = L(2L - 1)\alpha_t(v, L). \quad (26)$$

Compare with the discussion in Ref. [16].

In  $\text{H}_2^+$ , the stretched states are  $|vLn_s\rangle \equiv |v, L, I = 1, S = 3/2, J = L + 3/2, J_z = \pm(L + 3/2)\rangle$ . The same result Eq. (26) is obtained.

By evaluating the polarizabilities of all hyperfine states, we find that if  $L > 1$ , the largest value of  $\langle m | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | m \rangle$  within a rovibrational level occurs for the stretched states (see tables below). Therefore, in the following discussion, we normalize the polarizability anisotropy values of any hyperfine state in a particular rovibrational level relative to that of the stretched states in that same level.

For  $\text{HD}^+$ , combining the result Eq. (26) for the stretched states with the approximate behavior Eq. (12), we obtain  $\langle vLn_s | \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp} | vLn_s \rangle \propto (3 + 5L + 2L^2)^{-1}$ . This describes a rather strong decrease in the magnitude of all anisotropic polarizability values, not only those of the stretched states, with increasing  $L$ .

#### IV. NUMERICAL RESULTS FOR HYPERFINE-STATE DEPENDENCE

The evaluation of the matrix elements of Eq. (10) for all (exact) hyperfine states is straightforward, once the hyperfine states in absence of electric field are known. The calculation can for example proceed by considering the expansion of the hyperfine states in pure states, and then applying Eq. (25), which holds for the pure states of any molecular hydrogen ion. Actually, the matrix elements are the same (apart from prefactors such as  $\alpha_t$ ) as the matrix elements for the electric quadrupole shift evaluated in Ref. [16], and an explicit formula is given there.

We have performed the computation for the rovibrational levels up to  $v = 4$  and  $L = 4$ . Note that the polarizability anisotropy vanishes for  $L = 0$  states and is therefore not reported in the tables. We confine ourselves to the case of zero magnetic field.

The results are summarized in Tables V and VI where we give the values for the hyperfine states having  $J_z = 0$ . The values for  $J_z \neq 0$  can be easily obtained using Eq. (20). Note that for a given hyperfine state and value of  $L$  the dependence on  $v$  is usually weak, limited to several percent, except for a few cases.

By looking at the values in the Tables V, VI, one can see that the approximation that the polarizability does not depend on  $F$  is quite good for some hyperfine states, and moderate in others, which is due to their more-or-less pure character. A main result of the analysis is therefore that in order to obtain values accurate to better than one atomic unit for  $\text{HD}^+$ , because of its large values of  $\alpha_t$ , it is necessary to use the exact hyperfine dependence of the polarizability anisotropy.

The results for  $\text{H}_2^+$  in odd- $L$  states are shown in Table VII. We can see that in this species, the anisotropic polarizabilities are always very close to those of the pure states. The maximum deviation is approximately 0.01 atomic unit. Thus, for current purposes, for  $\text{H}_2^+$  one may use Eq. (25) for all rovibrational levels.

#### V. BLACKBODY RADIATION FREQUENCY SHIFT

##### A. Generalities

The blackbody radiation shift of a level  $m$  is computed as

$$\Delta E_{\text{BBR}}(m, T) = -\frac{1}{2} \int_0^{\infty} \alpha_s(m, \omega) \mathcal{E}_{\text{BBR}}(T, \omega)^2 d\omega, \quad (27)$$

if the BBR electric field  $\mathcal{E}_{\text{BBR}}$  is unpolarized. The contributions from the magnetic field are neglected. Therefore, under this assumption and because of the small hyperfine splittings compared to the (smallest) rotational levels splitting (20 MHz

TABLE VI. Same as Table V, but for levels  $L = 2, 3, 4$ . Note that the values in the second column are rounded.

Hyp. state ( $F, S, J, J_z$ )	Eq. (25) (normalized)	Level ( $v, L$ )				
		$(v, L) = (0, 2)$	$(v, L) = (1, 2)$	$(v, L) = (2, 2)$	$(v, L) = (3, 2)$	$(v, L) = (4, 2)$
(0,1,3,0)	-0.8	-0.799487	-0.799517	-0.799548	-0.799578	-0.799608
(0,1,2,0)	-0.5	-0.499349	-0.49939	-0.49943	-0.499469	-0.499508
(0,1,1,0)	-0.7	-0.698944	-0.699011	-0.699076	-0.699141	-0.699205
(1,0,2,0)	-1	-0.89668	-0.902108	-0.907625	-0.913227	-0.918913
(1,1,1,0)	-0.7	-0.598522	-0.605382	-0.612152	-0.618825	-0.625393
(1,1,2,0)	-0.5	-0.572569	-0.56875	-0.564853	-0.560883	-0.556839
(1,1,3,0)	-0.8	-0.798847	-0.798904	-0.798961	-0.799019	-0.799079
(1,2,0,0)*	0	0	0	0	0	0
(1,2,1,0)	0.7	0.597466	0.604392	0.611229	0.617966	0.624598
(1,2,2,0)	0.2143	0.182884	0.184534	0.186194	0.187865	0.189546
(1,2,3,0)	-0.2	-0.201666	-0.201579	-0.201491	-0.201403	-0.201313
(1,2,4,0)*	-0.7143	-0.714286	-0.714286	-0.714286	-0.714286	-0.714286
		$(v, L) = (0, 3)$	$(v, L) = (1, 3)$	$(v, L) = (2, 3)$	$(v, L) = (3, 3)$	$(v, L) = (4, 3)$
(0,1,4,0)	-0.7143	-0.713807	-0.713835	-0.713864	-0.713892	-0.71392
(0,1,3,0)	-0.6	-0.599383	-0.599421	-0.599459	-0.599496	-0.599533
(0,1,2,0)	-0.6857	-0.684872	-0.684925	-0.684977	-0.685028	-0.685079
(1,0,3,0)	-0.8	-0.743487	-0.745805	-0.748206	-0.750693	-0.753272
(1,1,2,0)	-0.6857	-0.641563	-0.644157	-0.646756	-0.649358	-0.651959
(1,1,3,0)	-0.6	-0.638925	-0.637509	-0.636019	-0.634449	-0.632793
(1,1,4,0)	-0.7143	-0.712034	-0.712155	-0.712277	-0.712399	-0.712523
(1,2,1,0)*	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48
(1,2,2,0)	-0.1714	-0.216421	-0.213776	-0.211124	-0.208471	-0.205819
(1,2,3,0)	-0.2533	-0.271538	-0.270598	-0.26965	-0.268696	-0.267735
(1,2,4,0)	-0.4286	-0.431302	-0.431152	-0.431002	-0.430852	-0.4307
(1,2,5,0)*	-0.6667	-0.666667	-0.666667	-0.666667	-0.666667	-0.666667
		$(v, L) = (0, 4)$	$(v, L) = (1, 4)$	$(v, L) = (2, 4)$	$(v, L) = (3, 4)$	$(v, L) = (4, 4)$
(0,1,5,0)	-0.6667	-0.666213	-0.66624	-0.666267	-0.666293	-0.66632
(0,1,4,0)	-0.6071	-0.606572	-0.606607	-0.606642	-0.606676	-0.60671
(0,1,3,0)	-0.6548	-0.654035	-0.654081	-0.654126	-0.65417	-0.654214
(1,0,4,0)	-0.7143	-0.677583	-0.678822	-0.68012	-0.68148	-0.682906
(1,1,3,0)	-0.6548	-0.627904	-0.62934	-0.630793	-0.632265	-0.633749
(1,1,4,0)	-0.6071	-0.630532	-0.629989	-0.62939	-0.628733	-0.628016
(1,2,2,0)*	-0.5612	-0.561224	-0.561224	-0.561224	-0.561224	-0.561224
(1,1,5,0)	-0.6667	-0.663695	-0.663856	-0.664019	-0.664183	-0.664348
(1,2,3,0)	-0.3929	-0.420442	-0.41896	-0.417462	-0.415946	-0.414418
(1,2,4,0)	-0.4096	-0.423439	-0.422708	-0.421974	-0.421236	-0.420494
(1,2,5,0)	-0.5	-0.503426	-0.503237	-0.503047	-0.502857	-0.502666
(1,2,6,0)*	-0.6364	-0.636364	-0.636364	-0.636364	-0.636364	-0.636364

versus 1 THz, i.e.,  $2 \times 10^{-5}$  in relative terms), the BBR shift is to a high approximation equal for all hyperfine states of a given rovibrational level.

## B. Approximate treatment

### 1. Homonuclear ions

We may approximate the polarizability of the homonuclear ions by its zero-frequency value:  $\alpha_s((v, L), \omega) \simeq \alpha_s((v, L), \omega = 0) = \alpha_s(v, L)$ , where the values are given in the Tables II and III above. Then

$$\begin{aligned} \Delta E_{\text{BBR}}(m, T) &\simeq \Delta E_{\text{stat}}((v, L), T) \\ &= -\frac{1}{2} \alpha_s((v, L), 0) (831.9 \text{ V/m})^2 (T/300 \text{ K})^4. \end{aligned} \quad (28)$$

(In this expression, the value of  $\alpha_s$  in atomic units is to be multiplied by the value of  $4\pi\epsilon_0 a_0^3$  in SI units.) A polarizability of one atomic unit gives a frequency shift of  $-8.6$  mHz at 300 K. The shifts of several selected rovibrational levels are given in Table VIII.

### 2. Heteronuclear ions

For the heteronuclear ions, we express the polarizability as

$$\begin{aligned} \alpha_s((v, L), \omega) &= \alpha_s((v, L), 0) + \delta\alpha_{s, \text{dyn,rv}}((v, L), \omega) \\ &\quad + \delta\alpha_{s, \text{dyn,elec}}((v, L), \omega). \end{aligned} \quad (29)$$

$\alpha_s((v, L), 0)$  is the variational calculation result. Here,  $\delta\alpha_{s, \text{dyn,elec}}((v, L), \omega)$  is the frequency-dependent contribution from the excited electronic levels. It does not include the



TABLE VII. Anisotropic polarizability of the states of  $\text{H}_2^+$  in  $L = 1, 3$  normalized to those of the stretched states and divided by  $(1 - 3J_z^2/[J(J+1)])$ . Second column: approximate value (value corresponding to the dominant pure component). Columns 3 to 7: exact result. States with an asterisk are pure states.

Hyp. state ( $I, S, J, J_z$ )	Eq. (25) (normalized)	Level ( $v, L$ )				
		$v = 0$	$v = 1$	$v = 2$ $L = 1$	$v = 3$	$v = 4$
$(1, \frac{1}{2}, \frac{3}{2}, J_z)$	-1.25	-1.24946	-1.2495	-1.24951	-1.24956	-1.2496
$(1, \frac{1}{2}, \frac{1}{2}, J_z)$	-0.125	-0.1216	-0.12186	-0.12212	-0.12238	-0.12262
$(1, \frac{3}{2}, \frac{1}{2}, J_z)$	2.125	2.12158	2.12185	2.12212	2.12239	2.12262
$(1, \frac{3}{2}, \frac{3}{2}, J_z)^*$	-0.875	-0.875	-0.875	-0.875	-0.875	-0.875
$(1, \frac{3}{2}, \frac{3}{2}, J_z)$	1	0.99946	0.9995	0.99952	0.99956	0.9996
$L = 3$						
$(1, \frac{1}{2}, \frac{7}{2}, J_z)$	-0.75	-0.74955	-0.74958	-0.74961	-0.74964	-0.74967
$(1, \frac{1}{2}, \frac{5}{2}, J_z)$	-0.75	-0.74871	-0.7488	-0.7489	-0.74899	-0.74909
$(1, \frac{3}{2}, \frac{3}{2}, J_z)^*$	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6
$(1, \frac{3}{2}, \frac{5}{2}, J_z)$	-0.4125	-0.41379	-0.41369	-0.41359	-0.4135	-0.41341
$(1, \frac{3}{2}, \frac{7}{2}, J_z)$	-0.5	-0.50044	-0.50041	-0.50038	-0.50035	-0.50032
$(1, \frac{3}{2}, \frac{9}{2}, J_z)^*$	-0.6875	-0.6875	-0.6875	-0.6875	-0.6875	-0.6875

frequency-independent part, which is instead included in  $\alpha_s((v, L), 0)$ . Both  $\delta\alpha_{s, \text{dyn,elec}}((v, L), \omega)$  and  $\delta\alpha_{s, \text{dyn,rv}}((v, L), \omega)$  are defined so that they vanish at  $\omega = 0$ . The frequency-dependent contributions from  $E1$  rovibrational transitions within the ground electronic state give rise to [17]

$$\begin{aligned} \delta\alpha_{s, \text{dyn,rv}}((v, L), \omega) &= \frac{1}{3} \frac{1}{2L+1} \sum_{v', L'} | \langle v' L' | \mathbf{d} | v, L \rangle |^2 \\ &\times \left( \frac{1}{E_{v' L'} - E_{vL} + \hbar\omega} + \frac{1}{E_{v' L'} - E_{vL} - \hbar\omega} \right. \\ &\left. - \frac{2}{E_{v' L'} - E_{vL}} \right). \end{aligned} \quad (30)$$

In this sum, the value of  $L'$  can only take on the values  $L \pm 1$ , due to the selection rule.

As a first approximation, we can neglect  $\delta\alpha_{s, \text{dyn,elec}}$ , as done above for the homonuclear ions, since the transitions to the excited electronic states are of similar character. This neglect will be corrected in the next section.

TABLE VIII. Static approximation of BBR shift and dynamic contribution of some levels of  $\text{H}_2^+$  at  $T = 300$  K. The total BBR shift is obtained by adding the values in the third and fourth columns.

$v$	$L$	$\Delta E_{\text{stat}}((v, L), T)$ [mHz]	$\Delta E_{\text{dyn,elec}}((v, L), T)$ [mHz]
0	0	-27.3	-0.0023
0	1	-27.4	-0.0023
0	3	-27.8	-0.0024
1	1	-33.7	-0.0044
1	3	-34.2	-0.0046
2	1	-41.7	
3	1	-51.9	-0.0156

The total BBR shift is

$$\begin{aligned} \Delta E_{\text{BBR}}((v, L), T) &= \Delta E_{\text{stat}}((v, L), T) + \Delta E_{\text{dyn,rv}}((v, L), T) \\ &+ \Delta E_{\text{dyn,elec}}((v, L), T). \end{aligned} \quad (31)$$

We first discuss the dynamic *rovibrational* contribution to the BBR shift,

$$\begin{aligned} \Delta E_{\text{dyn,rv}}((v, L), T) &= -\frac{1}{2} \int_0^\infty \delta\alpha_{s, \text{dyn,rv}}((v, L), \omega) \mathcal{E}_{\text{BBR}}(T, \omega)^2 d\omega, \end{aligned}$$

which we have computed for levels up to  $v_{\text{max}} = 10$ ,  $L_{\text{max}} = 5$ , extending the results of Ref. [17], which considered levels with  $v_{\text{max}} = 7$ ,  $L_{\text{max}} = 1$ .

In this computation, it is important to use the most accurate transition dipoles values available, in order to reach a sufficient absolute accuracy in the polarizability and BBR shift, since partial cancellations occur in Eq. (30). For  $v < 6, L < 6$  we use the precise transition dipoles of Tian *et al.* [35], based on variational wave functions. Their fractional inaccuracy is stated as smaller than  $1 \times 10^{-6}$  and is less than that of our previously published values in Ref. [14]. As a check, we have recomputed the transition dipole moment of  $(v = 0, L = 0) \rightarrow (v' = 0, L' = 1)$  with a larger basis set, and the value 0.342 833 4 a.u. in agreement with Tian *et al.* to better than  $3 \times 10^{-7}$  in fractional terms. We have computed the transition dipole moments between  $L = 5$  and  $L' = 6$  levels having  $v, v' < 6$  in order to extend the results of Tian *et al.* They are listed in Table IX. For larger  $v, v' \geq 6$  we use the Born-Oppenheimer transition dipole elements given in Ref. [25]. These agree, in the  $v, L$  range computed by Tian *et al.*, within one to two parts in  $10^4$  with their results. As energy differences  $E_{v, L} - E_{v', L'}$  we use the precise energies including QED corrections [36,37] when  $v < 5, L < 5$ , and otherwise the values of Moss [38].

TABLE IX. Selected reduced transition dipole matrix elements,  $d = \langle v'L' || \mathbf{d} || vL \rangle$ , for transitions between rovibrational states of  $\text{HD}^+$  for the case  $L = 5 \rightarrow L' = 6$  (in atomic units). The notation  $[x]$  means  $\times 10^x$ .

$v \rightarrow v'$	$d$	$v \rightarrow v'$	$d$
(0 $\rightarrow$ 0)	0.85382285	(3 $\rightarrow$ 0)	0.22598012[-02]
(0 $\rightarrow$ 1)	0.64170498[-01]	(3 $\rightarrow$ 1)	0.19539417[-01]
(0 $\rightarrow$ 2)	0.97751608[-02]	(3 $\rightarrow$ 2)	0.20027036
(0 $\rightarrow$ 3)	0.23604947[-02]	(3 $\rightarrow$ 3)	1.00176877
(0 $\rightarrow$ 4)	0.74298137[-03]	(3 $\rightarrow$ 4)	0.12862769
(0 $\rightarrow$ 5)	0.27963915[-03]	(3 $\rightarrow$ 5)	0.30336340[-01]
(1 $\rightarrow$ 0)	0.11178434	(4 $\rightarrow$ 0)	0.63859280[-03]
(1 $\rightarrow$ 1)	0.90139089	(4 $\rightarrow$ 1)	0.45000014[-02]
(1 $\rightarrow$ 2)	0.90803829[-01]	(4 $\rightarrow$ 2)	0.27891731[-01]
(1 $\rightarrow$ 3)	0.16798347[-01]	(4 $\rightarrow$ 3)	0.23541895
(1 $\rightarrow$ 4)	0.46309897[-02]	(4 $\rightarrow$ 4)	1.05507688
(1 $\rightarrow$ 5)	0.16105915[-02]	(4 $\rightarrow$ 5)	0.14394208
(2 $\rightarrow$ 0)	0.11198057[-01]	(5 $\rightarrow$ 0)	0.22302649[-03]
(2 $\rightarrow$ 1)	0.16073279	(5 $\rightarrow$ 1)	0.14049130[-02]
(2 $\rightarrow$ 2)	0.95063090	(5 $\rightarrow$ 2)	0.71058396[-02]
(2 $\rightarrow$ 3)	0.11129675	(5 $\rightarrow$ 3)	0.36420347[-01]
(2 $\rightarrow$ 4)	0.23608027[-01]	(5 $\rightarrow$ 4)	0.26815005
(2 $\rightarrow$ 5)	0.72022091[-02]	(5 $\rightarrow$ 5)	1.11088687

Table X (a) presents the relative value of the dynamic rovibrational contribution. We see that for the  $L = 0$  levels a strong cancellation between the (particularly large) contributions  $\Delta E_{\text{stat}}(v, L = 0, T)$  and  $\Delta E_{\text{dyn,rv}}(v, L = 0, T)$  occurs, which results in a small BBR shift. In absolute terms, the BBR shift value is seen to grow with  $v$  and with  $L$ ; see part (b) of the table. The absolute values are in the range of 1 mHz to several tens of mHz, for  $v = 0, \dots, 6$  and moderate  $L$ .

For  $v < 6$  we estimate the inaccuracy of  $\Delta E_{\text{dyn,rv}}(v, L, 300 \text{ K})$  to be less than  $10^{-7}$  Hz, since the individual contributions to the sum are less than 0.1 Hz in absolute value. The values of  $\Delta E_{\text{stat}}(v, L, 300 \text{ K})$  are smaller than 0.1 Hz in absolute value, and their inaccuracy is determined by the inaccuracy of our  $\alpha_s(v, L, \omega = 0)$  values. The inaccuracy is thus less than  $10^{-6}$  Hz. However, the nonrelativistic approximation implies that both  $\alpha_s(v, L, \omega = 0)$  and the transition dipoles are only accurate to the  $1 \times 10^{-4}$  fractional level. Then, the theoretical inaccuracy of the BBR shift, assuming the last term in Eq. (31) is negligible, may be stated conservatively as less than  $3 \times 10^{-5}$  Hz for the levels  $v < 6$ , since the shift and its uncertainty is mostly determined by three contributions, each with approximate uncertainty of  $1 \times 10^{-5}$  Hz. For  $v \geq 6$ , taking into account that the transition dipoles values are calculated in Born–Oppenheimer approximation, the overall inaccuracy is estimated at  $6 \times 10^{-5}$  Hz.

From an experimental point of view, the temperature derivative of the BBR shift is an important quantity, since the temperature of the BBR field in an ion trap has a relatively large uncertainty, due to the difficulty in determining it experimentally. For  $\text{H}_2^+$  this derivative can be trivially obtained from Eq. (28), while the results for  $\text{HD}^+$  are given in Tables X(c) and X(d). We find a strong variation between levels. Only for levels having larger  $v$  and  $L$  the normalized

TABLE X. (a) Values of the dynamic vibrational contribution to the BBR shift of a level  $(v, L)$  of  $\text{HD}^+$  normalized to the static contribution  $\Delta E_{\text{dyn,rv}}(v, L, T)/\Delta E_{\text{stat}}(v, L, T)$  at  $T = 300 \text{ K}$ . (b) Approximate total BBR shift  $\Delta E_{\text{stat}}(v, L, T) + \Delta E_{\text{dyn,rv}}(v, L, T)$  in Hz. (c) Temperature derivatives of the approximate total BBR shift  $d[\Delta E_{\text{stat}}(v, L, T) + \Delta E_{\text{dyn,rv}}(v, L, T)]/dT$  at 300 K and in mHz/K. (d) Normalized temperature derivative of the total BBR shift  $(T/4)(\Delta E_{\text{stat}} + \Delta E_{\text{dyn,rv}})^{-1}d(\Delta E_{\text{stat}} + \Delta E_{\text{dyn,rv}})/dT$  at 300 K. These results are nonrelativistic and do not include the frequency-dependent contributions  $\Delta E_{\text{dyn,elec}}$  from excited electronic states, which are given in Table XI.

$v$	$L$					
	0	1	2	3	4	5
(a)						
0	-1.0025	-1.1333	-0.9720	-0.7993	-0.6340	-0.4865
1	-1.0014	-1.0468	-0.9087	-0.7593	-0.6148	-0.4844
2	-1.0004	-0.9606	-0.8436	-0.7154	-0.5902	-0.4761
3	-0.9994	-0.8754	-0.7769	-0.6682	-0.5609	-0.4621
4	-0.9983	-0.7917	-0.7098	-0.6186	-0.5277	-0.4432
5	-0.9973	-0.7104	-0.6431	-0.5674	-0.4913	-0.4199
6	-0.9959	-0.6322	-0.5769	-0.5153	-0.4532	-0.3925
7	-0.9948	-0.5567	-0.5132	-0.4636	-0.4120	-0.3645
8	-0.9935	-0.4864	-0.4520	-0.4121	-0.3713	-0.3330
9	-0.9921	-0.4200	-0.3941	-0.3635	-0.3312	-0.2996
10	-0.9905	-0.3596	-0.3385	-0.3173	-0.2918	-0.2672
(b)						
0	0.0084	0.0046	-0.0010	-0.0070	-0.0129	-0.0183
1	0.0057	0.0019	-0.0037	-0.0099	-0.0160	-0.0216
2	0.0019	-0.0019	-0.0075	-0.0138	-0.0201	-0.0261
3	-0.0034	-0.0071	-0.0128	-0.0192	-0.0257	-0.0319
4	-0.0106	-0.0143	-0.0200	-0.0265	-0.0332	-0.0397
5	-0.0203	-0.024	-0.0297	-0.0364	-0.0433	-0.0502
6	-0.0353	-0.0372	-0.0431	-0.0498	-0.0570	-0.0644
7	-0.0531	-0.0554	-0.0612	-0.0682	-0.0758	-0.0834
8	-0.0780	-0.0802	-0.0863	-0.0937	-0.1017	-0.1100
9	-0.1123	-0.1151	-0.1213	-0.1290	-0.1379	-0.1475
10	-0.1609	-0.1645	-0.1715	-0.1795	-0.1897	-0.2009
(c)						
0	-0.12	-0.13	-0.15	-0.17	-0.19	-0.22
1	-0.18	-0.18	-0.20	-0.22	-0.25	-0.28
2	-0.24	-0.25	-0.27	-0.29	-0.31	-0.35
3	-0.33	-0.34	-0.35	-0.38	-0.4	-0.44
4	-0.44	-0.45	-0.47	-0.49	-0.52	-0.55
5	-0.59	-0.60	-0.62	-0.64	-0.67	-0.71
6	-0.81	-0.79	-0.81	-0.84	-0.87	-0.92
7	-1.07	-1.05	-1.08	-1.11	-1.15	-1.19
8	-1.42	-1.41	-1.43	-1.47	-1.52	-1.57
9	-1.89	-1.89	-1.92	-1.97	-2.02	-2.10
10	-2.56	-2.58	-2.62	-2.67	-2.74	-2.84
(d)						
0	-1.11	-2.14	11.27	1.79	1.12	0.91
1	-2.32	-7.23	3.99	1.66	1.15	0.95
2	-9.61	9.94	2.64	1.56	1.17	0.99
3	7.39	3.55	2.07	1.47	1.18	1.02
4	3.16	2.37	1.75	1.39	1.17	1.05
5	2.18	1.87	1.55	1.32	1.16	1.06
6	1.72	1.60	1.42	1.26	1.15	1.07
7	1.50	1.43	1.32	1.22	1.13	1.07
8	1.36	1.32	1.24	1.18	1.12	1.07
9	1.27	1.23	1.19	1.14	1.10	1.07
10	1.20	1.18	1.15	1.11	1.09	1.06

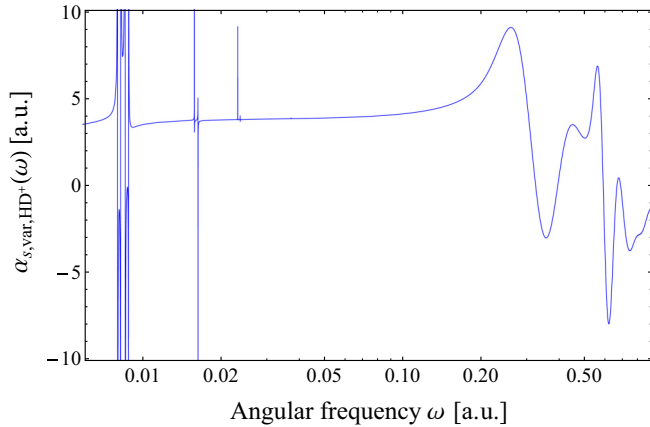


FIG. 1. (Color online) The scalar polarizability of  $\text{HD}^+$  in the level ( $v = 1, L = 1$ ), computed using variational wave functions. Atomic units are used.

derivative is close to the value  $4/T$  corresponding to a purely static BBR shift [Eq. (28)].

### C. Variational results

For several levels of both  $\text{H}_2^+$  and  $\text{HD}^+$  we have computed the dynamic polarizability  $\alpha_{s,\text{var}}(\omega)$  [and  $\alpha_{t,\text{var}}(\omega)$ ] *directly*, using variational wave functions. For one particular level of  $\text{HD}^+$ , the polarizability  $\alpha_s$  has been computed up to large frequencies; see Fig. 1. The calculation was performed using the complex coordinate rotation method [39,40]. This overview clearly shows the dominating contributions from the rovibrational levels when  $\omega$  is small whereas for large  $\omega$  the excited electronic states yield broad dispersive resonances. The low-frequency tail of these resonances, as  $\omega \rightarrow 0$ , is responsible for giving rise to  $\Delta E_{\text{dyn,elec}}$ .

For several other levels, the computation was performed up to an angular frequency  $\omega = 0.1$  atomic units, in steps of  $10^{-5}$  atomic units. The results are given in the Supplementary Material [41]. Since the computation was done in the nonrelativistic approximation, the fractional inaccuracy of the values with respect to the exact values is approximately  $1 \times 10^{-4}$ . This is then also the fractional inaccuracy of the BBR shifts computed from this data.

#### I. $\text{H}_2^+$

For  $\text{H}_2^+$ , we can compare our values of the scalar polarizability with the calculation by Pilon, who has communicated the values at six different frequencies [42]. The values agree, with deviations of at most  $2 \times 10^{-6}$  atomic units in the range  $\omega \leq 0.08$ .

We show in Fig. 2 the frequency-dependent part of the polarizability of one level of  $\text{H}_2^+$ ,  $\alpha_{s,\text{var},\text{H}_2^+}((1,1),\omega) - \alpha_{s,\text{var},\text{H}_2^+}((1,1),0)$ , at low frequencies. For the computation of the BBR shift at 300 K, frequencies up to approximately  $\omega = 0.013$  atomic units are relevant. In this range the polarizability is quite close to quadratic in  $\omega$ . With increasing vibrational quantum numbers  $v$ , the deviations from quadratic are more pronounced.

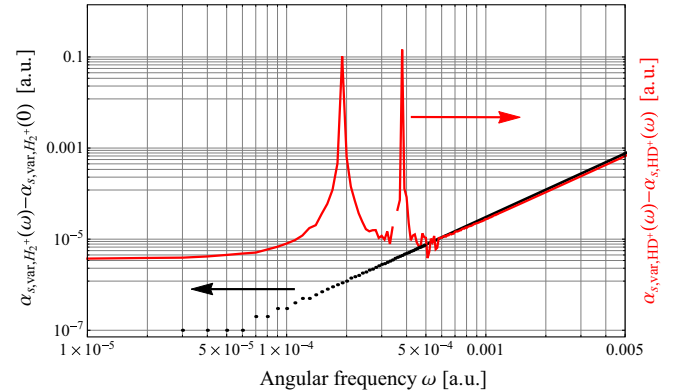


FIG. 2. (Color online) Black (dotted line) shows the frequency-dependent contribution of the scalar polarizability of  $\text{H}_2^+$  in the level ( $v = 1, L = 1$ ) computed using variational wave functions. Red (gray, full line) shows difference between the scalar polarizability of  $\text{HD}^+$ , also in the level ( $v = 1, L = 1$ ), computed variationally and approximately. Atomic units are used. The difference is noticeable close to the two rotational transition frequencies ( $v = 1, L = 1$ )  $\rightarrow$  ( $v = 1, L = 0$ ) and ( $v = 1, L = 1$ )  $\rightarrow$  ( $v = 1, L = 2$ ). A gap occurs in the red curve at  $\omega = 3.5 \times 10^{-4}$  atomic units because the difference is negative.

The dynamic electronic BBR shift corrections  $\Delta E_{\text{dyn,elec}}$  computed from the variational data [with an integration analogous to Eq. (27)] are shown in Table VIII. We see that the correction is small in relative terms,  $1 \times 10^{-4}$  for  $v = 0$ , increasing to  $4 \times 10^{-4}$  for  $v = 3$ . It is very weakly dependent on  $L$ . Nevertheless, these results show that the dynamic contribution should not be omitted even within the nonrelativistic approximation. When it is included, the overall inaccuracy is limited by the nonrelativistic approximation to approximately  $1 \times 10^{-4}$  fractionally. For  $v < 6$ ,  $L < 6$  the total BBR shift is smaller than 0.1 Hz. Therefore, the absolute error is less than 0.01 mHz.

#### 2. $\text{HD}^+$

For  $\text{HD}^+$ , a comparison of the variational dynamic polarizability  $\alpha_{s,\text{var},\text{HD}^+}(\omega)$  with the approximation  $\alpha_{s,\text{HD}^+}(\omega) = \alpha_s(\omega = 0) + \delta\alpha_{s,\text{dyn,rv}}(\omega)$  is depicted in Fig. 2, which shows their difference. In evaluating the approximation, we have used both the transition dipoles of Tian *et al.* [35] and their nonrelativistic energies, since also the variational polarizability was computed in the nonrelativistic approximation. The agreement is very good, except for small deviations near the transition frequencies (whose nominal contribution to the BBR shift is only of order  $1.5 \times 10^{-3}$  mHz), and a frequency-dependent contribution from the excited electronic states, which is again closely quadratic in frequency.

We fit the difference  $\alpha_{s,\text{var}}(\omega) - \alpha_{s,\text{HD}^+}(\omega)$  between variational and approximate frequency-dependent polarizability over the frequency range  $\omega_{\text{min}}(v, L)$  to 0.05 a.u. by a polynomial of the form given in Table XI. Here,  $\omega_{\text{min}}(v, L)$  is chosen appropriately so as to allow an accurate fit. These fits represent an approximation to  $\delta\alpha_{s,\text{dyn,elec}}(v, L, \omega)$  for frequencies from 0 to 0.05 a.u. The contribution of the cubic term is seen to be small compared to the quadratic one for the range of

TABLE XI. Fourth column: polynomial approximation to  $\alpha_{s,\text{dyn,elec}}(\omega)$ , the frequency-dependent part of the contribution to the polarizability  $\alpha_s$  of  $\text{HD}^+$  stemming from the excited electronic states. Fifth column: corresponding contribution to the BBR shift at 300 K. The angular frequencies  $\omega$  and  $\omega_{\min}$  are in atomic units.

$v$	$L$	$\omega_{\min}(v,L)$	Fit	$\Delta E_{\text{dyn,elec}}((v,L),T)$ [mHz]
0	0	0.0015	$16.10 \omega^3 + 14.54 \omega^2$	-0.0021
0	1	0.0015	$16.24 \omega^3 + 14.62 \omega^2$	-0.0021
0	3	0.002	$16.94 \omega^3 + 15.01 \omega^2$	-0.0022
0	4	0.003	$17.58 \omega^3 + 15.32 \omega^2$	-0.0022
1	1	0.0015	$48.34 \omega^3 + 24.76 \omega^2$	-0.0036
1	5	0.019	$63.87 \omega^3 + 25.86 \omega^2$	-0.0038
2	4	0.02	$148.1 \omega^3 + 42.73 \omega^2$	-0.0063
2	5	0.019	$166.0 \omega^3 + 42.92 \omega^2$	-0.0064
3	2	0.04	$395.8 \omega^3 + 62.68 \omega^2$	-0.0094

frequencies relevant for the BBR shift at 300 K. Table XI gives the corresponding contributions to the BBR shift, to be added to the other two contributions given in Table X. The error in the values of  $\Delta E_{\text{dyn,elec}}$  due to this fit treatment is on the order of 0.001 mHz. We see that this BBR shift contribution again varies weakly with  $L$ , but significantly with  $v$  and that for levels with  $v = 3$  it reaches  $1 \times 10^{-5}$  Hz. Therefore, it needs to be taken into account even within the nonrelativistic approximation, if no loss of accuracy is desired. When this is done, the total error of the BBR shift due to the nonrelativistic approximation is expected to be  $1 \times 10^{-4}$  fractionally, or less than 0.03 mHz for the low-lying levels of  $\text{HD}^+$ ,  $v < 6$ .

## VI. CONCLUSION

We computed the nonadiabatic static polarizabilities of the molecular hydrogen ions  $\text{HD}^+$ ,  $\text{H}_2^+$ , and  $\text{D}_2^+$ , extending significantly previous results, mostly limited to rovibrational levels with rotational angular momentum  $L = 0, 1$ . For a num-

ber of rovibrational levels, we also computed the frequency-dependent nonadiabatic polarizability.

The dependence of the polarizability on the hyperfine state is derived and discussed in detail. We pointed out the special case of the pure states, for which a simple analytical result was derived. This result is actually a very good approximation for all hyperfine states of  $\text{H}_2^+$ . The hyperfine-state dependence is of crucial importance if a detailed understanding of the systematic shifts of transition frequencies is to be performed.

We also computed the shifts induced by the blackbody radiation field, and their temperature derivatives.

Emphasis has been given here to high numerical accuracy. The effective relative inaccuracy of our computed values is about  $1 \times 10^{-4}$  due to the neglect of relativistic corrections. For  $\text{H}_2^+$  and  $\text{D}_2^+$  this translates in an absolute inaccuracy of 0.001 a.u. for all levels with  $v < 6$ ,  $L < 5$ . For  $\text{HD}^+$  in  $L = 0, 1$  levels the inaccuracy is less than 0.1 a.u., and in  $L \geq 2$ , it is less than 0.003 a.u. An inaccuracy of 0.1 atomic units is sufficiently small to allow the Stark shift to be evaluated with a theoretical error corresponding to the  $10^{-18}$  fractional-frequency level, given the typical electric-field values in ion traps.

In order to obtain accurate values of the blackbody radiation shift, we used accurate values of the transition dipoles and analyzed the importance of the contributions from excited electronic states. We estimate the inaccuracy of the shifts to be less than 0.03 mHz for levels with  $v < 6$ ,  $L < 6$ , at 300 K, for both  $\text{HD}^+$  and  $\text{H}_2^+$ . This corresponds to theoretical fractional-frequency errors on the order of  $1 \times 10^{-18}$ .

Using the present results it becomes possible to identify theoretically transitions having low sensitivity to external fields [16,26]. This represents an important aspect in the future spectroscopy of the simplest stable molecules.

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