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Search for the variation of fundamental constants: Strong enhancements in $X\ ^2\Pi$ cations of dihalogens and hydrogen halides

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We investigate a number of diatomic molecular ions to search for strongly enhanced effects of variation of fundamental constants important for physics beyond the standard model. The relative enhancements due to fine structure and electron-to-proton mass ratio variation occur in transitions between nearly degenerate levels of different nature. Since the trapping techniques for molecular ions have already been developed, the proposed molecules HBr^+, HI^+, ${Br_2}^+$, ${I_2}^+$, IBr^+, ICl^+, and IF^+ are very promising candidates for future high-resolution experiments.

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I. INTRODUCTION

Theories unifying gravity with the other interactions or extensions to the standard model suggest the possibility of spatial and temporal variation of dimensionless fundamental physical constants, such as the fine structure constant, $\alpha = e^2/\hbar c$, and the proton-to-electron mass ratio, $\mu = m_p/m_e$ [1–3], the latter being connected to the strong coupling constant [4,5] (and to a lesser extent to the fine-structure constant; e.g., see Ref. [6]). For example, dark matter scalar fields could couple to the standard model Lagrangian leading to changes in fundamental constants in space-time such as particle mass and the coupling for the gauge groups [7,8]. Several popular models also relate variation of the fundamental constants to the evolution of dark energy [1,3,9].

Two major directions for the search of α and μ variation are observational studies, such as the analyses of high-resolution quasar absorption spectra (Refs. [10–12], and references therein), and laboratory research, including atomic and molecular clocks [13,14]. While the former has clear advantage due to the large look-back time involved which is of the order of the age of our universe, the latter has a clear advantage from the vast selection of suitable atomic and molecular candidates and the control of the experimental setup using high-precision reference clocks.

Molecules are very promising probes for variation of fundamental constants (VFCs) as molecular spectra can be very sensitive to both α and μ [14–16], making it possible to look for variation of both constants in a single experiment. So far, the use of molecules has mostly focused on astrophysical observations of molecular spectra at high redshifts. Molecular probes used in astrophysical research include the Lyman and Werner absorption lines in H_2 and HD molecules [17,18], the 18 cm^{-1} transition of OH [19], the inversion spectrum of ammonia [20–22], Λ-doubling transitions of CH [23], and the internal rotational transitions of interstellar methanol [16,24].

The most stringent laboratory molecular limit to date on the variation of μ is $\dot{\mu}/\mu = (-3.8 \pm 5.6) \times 10^{-14}$ yr^{-1} [25], set in a two-year-long experiment over the course of which vibrational transitions in the SF_6 molecule were compared with the Cs standard. So far, this is the only laboratory experiment using molecular systems to study VFC [compare to the most recent experiment on Yb^+ with $\dot{\mu}/\mu = (-0.5 \pm 1.6) \times 10^{-16}$ yr^{-1} [26]]. Nevertheless, the development of methods for creation and trapping of ultracold molecules [27–29] opens exciting new prospects to test for VFC by means of high-resolution molecular spectroscopy. In such experiments it is important to use molecules that experience enhanced sensitivity to VFC. However, locating such favorable systems is not a trivial task.

Nearly degenerate levels with different sensitivity to VFC may provide huge enhancements of a relative variation, since $\delta\omega/\omega$ tends to infinity when the distance between the levels ω is close to zero. This is the case with dysprosium [10,30]. Relatively low accuracy of the transition frequency measurements in Dy provides record-high accuracy in VFC measurements [31]. However, the problem with Dy is that one of the levels has a short lifetime, thus limiting the accuracy.

Molecules can have both degenerate levels and very narrow transition widths. Diatomic molecules that have a near cancellation between hyperfine structure and rotational intervals [32], hyperfine structure and Λ doubling [33], or between fine-structure and vibrational intervals [34] can benefit from such an enhanced sensitivity. A number of such molecules have already been identified, e.g., Cs_2 [35,36], CaH, MgH, CaH^+ [37–39], ${Cl_2}^+$, IrC, HfF^+, SiBr, LaS, LuO, Sr_2, and others [32,34,40,41]. Several polyatomic molecules were suggested for laboratory studies of VFC as well (see, e.g., [42,43], and references in [14,16]). Here we note that practical advantage can be gained by using molecular ions rather than neutral molecules due to the greater ease of

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trapping and cooling [44,45]. Unfortunately, experimental spectroscopic constants for charged diatomics are scarce compared to their neutral counterparts, and the search for VFC using such molecules is somewhat limited.

In this work we investigate a group of diatomic molecules that satisfy all of the above mentioned criteria, namely, the singly charged dihalogens and hydrogen halides. We are interested in the forbidden rovibrational transitions between the nearly degenerate sublevels of the $X\,^2\Pi$ ground states of these molecules. Using available experimental spectroscopic data, we identify such promising transitions, and examine the dependence of the transition energy on both α and μ. Strong enhancement of the sensitivity of these transitions to variations in α and in μ makes them excellent candidates for future experiments to detect VFC.

II. SPECTROSCOPIC CONSTANTS

The systems presented here were selected for an in-depth study due to the availability of their accurate experimental spectroscopic parameters (as defined in Appendix A), which are listed in Table I. These systems include four isotopologues of HBr^+ ($H^{79}Br^+$, $H^{81}Br^+$, $D^{79}Br^+$, and $D^{81}Br^+$) [46,47], two isotopologues of HI^+ (HI^+ and DI^+) [48], three isotopologues of ${Br_2}^+$ (${^{79}Br_2}^+$, ${^{81}Br_2}^+$, and $^{79}Br^{81}Br^+$) [49], ${I_2}^+$ [50,51], two isotopologues of IBr^+ ($I^{79}Br^+$ and $I^{81}Br^+$) [52], two isotopologues of ICl^+ ($I^{35}Cl^+$ and $I^{37}Cl^+$) [53], and IF^+ [54]. Spectroscopic constants for DI^+ were obtained by isotopical scaling [55] from available experimental parameters for HI^+. We note, that the rotational constant B_e and vibrational-rotational coupling constant α_e are given for the $^2\Pi_{3/2}$ substate of ${I_2}^+$ only [51]; however, we use them for both $^2\Pi_\Omega$ substates. A number of other charged dihalogens and hydrogen halides were considered, but were found unsuitable for the present study. These systems are discussed in more detail in Appendix B.

In cases where experimental spectroscopic constants B_e, D_e, and α_e are not given explicitly, we estimated these from the known constants by the use of simple relations. The rotational constant B_e was calculated from the bond length R_e and the reduced mass M using the rigid-rotor relation,

$$B_e = \frac{\hbar}{4\pi c M R_e^2}. \tag{1}$$

For the centrifugal distortion constant D_e the Kratzer formula [56] was assumed,

$$D_e = \frac{4B_e^3}{\omega_e^2}. \tag{2}$$

Similarly, for the vibrational-rotational coupling constant α_e we used the Pekeris formula [57] derived from the Morse potential,

$$\alpha_e = \frac{6B_e^2}{\omega_e}\left(\sqrt{\frac{\omega_e x_e}{B_e}} - 1\right). \tag{3}$$

Expressions (1)–(3) were used for estimation of B_e, D_e, and α_e for systems IF^+, ICl^+, and IBr^+. In the case of IF^+ the bond lengths were experimental ($R_e = 1.836$ and 1.832 Å for $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, respectively [54]), and for ICl^+ and IBr^+ we computed the bond lengths using the DIRAC13 program

TABLE I. Experimental spectroscopic constants (in cm^{-1}) of the systems under study. Asterisk denotes values calculated from other constants using Eqs. (1)–(3).

	$H^{79}Br^+$	$H^{81}Br^+$	$D^{79}Br^+$	$D^{81}Br^+$	HI^+	${^{79}Br_2}^+$	$^{79}Br^{81}Br^+$	${^{81}Br_2}^+$	${I_2}^+$	$I^{79}Br^+$	$I^{81}Br^+$	$I^{35}Cl^+$	$I^{37}Cl^+$	IF^+
ω_e	2439.873(4)	2439.493(4)	1736.786(1)	1736.251(1)	2195.2435(8)	365.5(8)	363.05(30)	360.85(40)	234.5(20)	301.5(10)	300(1)	433.1(8)	433.1(8)	691.5(20)
$\omega_e x_e$	46.189(3)	46.174(3)	23.3553(8)	23.334(1)	39.5974(3)	1.07(15)	1.12(3)	1.10(8)	0.73(4)	1.5(1)	1.45(10)	1.714(8)	1.714(8)	2.1(5)
$\omega_e y_e$	0.2304(10)	0.2302(10)	0.0828(3)	0.0822(3)										
$\omega_e z_e \times 10^3$	−1.92(11)	−1.90(11)	−0.34(3)	−0.29(4)										
$B_e \times 10^2$	807.98(2)	807.72(2)	409.393(2)	409.145(3)	633.07(2)	8.86(7)	8.86(7)	8.86(7)	3.97773(8)	6.10(2)*	6.01(2)*	12.34(6)*	11.82(6)*	30.3(2)*
$\alpha_e \times 10^3$	242.0(2)	241.9(2)	87.66(2)	87.68(3)	175.39(4)	0.32(3)	0.32(3)	0.32(3)	0.1182(2)	0.29(2)*	0.28(2)*	0.575(4)*	0.543(4)*	1.3(3)*
$\gamma_e \times 10^4$	9.6(4)	9.5(4)	2.9(5)	3.34(9)	1.602(8)									
$\epsilon_e \times 10^5$					−6.62(1)									
$D_e \times 10^7$	3528(4)	3524(4)	900(50)	890(10)	2086.3(5)	0.208(6)*	0.211(5)*	0.214(6)*	0.0458(8)*	0.100(2)*	0.096(2)*	0.401(6)*	0.352(6)*	2.33(5)*
$\beta_e \times 10^7$	−30.2(14)	−30.3(14)			−2.7(7)									
A_e	−2652.66(3)	−2652.66(3)	−2652.35(5)	−2652.35(5)	−5359(6)	−2820(40)	−2820(40)	−2820(40)	−5197(4)	−4662(2)	−4662(2)	−4656.2(10)	−4656.2(10)	−5690(8)
$A^{(1)}$	2.061(3)	2.063(4)	1.9(1)	1.9(1)	5.2114(8)	5.0(8)	3.7(3)	3.9(4)	11(2)	3(1)	0(1)	−8.1(8)	−8.1(8)	9(2)
$A^{(2)}$	0.160(2)	0.159(2)				−0.11(15)	−0.03(3)	−0.06(8)	0.04(4)	1.0(1)	1.1(1)	0.734(8)	0.734(8)	−1.8(5)
$A^{(3)}$	0.0105(3)	0.0107(3)												
$A_D \times 10^3$	2.25(6)	2.22(7)			0.61(7)	−0.2(7)	−0.2(7)	−0.2(7)		0.241(2)*	0.237(2)*	−0.0553(4)*	−0.0529(4)*	−1.32(1)*
$A_D^{(1)} \times 10^5$	47(5)	52(6)			92.1(14)	2(3)	2(3)	2(3)		−0.16(3)*	−0.15(3)*	0.0339(5)*	0.0322(5)*	0.7(2)*
$A_D^{(2)} \times 10^3$	9.7(9)	9.1(9)												

TABLE II. Experimental Λ-doubling parameters (in cm^{-1}).

	$H^{79}Br^+$	$H^{81}Br^+$	HI^+
p_e	2.0780(18)	2.0846(12)	3.5203(17)
$p^{(1)} \times 10^2$	−2.68(16)	−2.64(15)	−4.98(3)
$p^{(2)} \times 10^3$	−1.3(3)	−1.4(3)	
$p_D \times 10^5$	−6.2(5)	−5.7(6)	−9.4(6)
$p_D^{(1)} \times 10^6$	−2.2(16)	−1.4(18)	
$q_e \times 10^3$	−6.5(4)	−6.3(4)	−3.8(3)
$q^{(1)} \times 10^4$	−9.5(4)	−9.9(4)	−2.6(6)
$q^{(2)} \times 10^4$	1.4(7)	1.6(7)	

package [58] through a fully relativistic four-component Fock-space coupled cluster (4c-FS-CCSD) method [59] with aug-cc-pVQZ basis sets [60,61] for Cl and Br and a Faegri dual basis set [62] for I. The resulting values used in this work are $R_e(^2\Pi_{3/2}) = 2.233$ Å, $R_e(^2\Pi_{1/2}) = 2.232$ Å for ICl^+ and $R_e(^2\Pi_{3/2}) = 2.381$ Å, $R_e(^2\Pi_{1/2}) = 2.385$ Å for IBr^+.

The effect of Λ doubling further splits the doubly degenerate rotational $^2\Pi_\Omega$ levels by a small energy difference, given as

$$\Delta E_{\mathrm{ef}}(^2\Pi_{1/2}) = (p_v + 2q_v)\left(J + \frac{1}{2}\right), \tag{4}$$

$$\Delta E_{\mathrm{ef}}(^2\Pi_{3/2}) = \left(\frac{p_v}{Y_v^2} + \frac{2q_v}{Y_v}\right)\left(J - \frac{1}{2}\right)\left(J + \frac{1}{2}\right)\left(J + \frac{3}{2}\right) \tag{5}$$

with $Y_v = A_v/B_v$ and the Λ-doubling parameters p_v and q_v having vibrational dependence analogous to Eq. (A6) and usually also the centrifugal distortion analogous to Eq. (A7). The split levels are labeled e/f according to their rotational symmetry in the nonalternating fashion (as opposed to the $+/-$ labels) [63].

In the case of HBr^+ and HI^+ the Λ doubling was resolved and described by experiment [47,48] and resulting experimental constants are given in Table II. Parameters for the deuterated isotopologues were obtained by isotopical scaling [55].

For the studied dihalogen cations Λ doubling was not observed in the experiment, since the resolution was not high enough. Hence we calculated the Λ-doubling parameters assuming the pure precession approximation (PPA) [64,65] as

$$p_v = \frac{4A_vB_v}{\Delta E_{\Sigma\Pi}}, \qquad q_v = \frac{4B_v^2}{\Delta E_{\Sigma\Pi}}, \tag{6}$$

where $\Delta E_{\Sigma\Pi}$ is the energy difference between the $X\,^2\Pi$ ground state and the nearest excited $^2\Sigma$ state, which accounts for the majority of the interaction.

For the closely related dihalogen ${Cl_2}^+$ the Λ-doubling parameters p_1 and p_2 were determined by experiment [66] to have values 0.0202 and 0.0200 cm^{-1}, respectively. These are reasonably well reproduced by the PPA expressions (6) with the corresponding values of −0.0226 and −0.0225 cm^{-1} (note that the sign only dictates the correct order of $+/-$ or e/f rotational symmetry levels, which were not assigned in the experiment). This justifies the use of the PPA for the studied dihalogen cations. The $B\,^2\Sigma^+_{(g)}$ excitation energies were determined using the DIRAC13 program package [58] using the FS-CCSD method with the Dyall's v3z basis set [67,68] in the exact two-component (X2C) formalism [69,70]. Resulting energies reproduce well the experimental values reported in Refs. [71,72], relative errors being less than 4% in all cases. We used the experimental excitation energies in Eq. (6) for ${Br_2}^+$ and ${I_2}^+$ and the theoretical values for IBr^+, ICl^+ (for which the experimental values were to some extent estimated), and IF^+ (for which no experimental value was available).

III. SENSITIVITY TO VARIATION OF α AND μ

Using available spectroscopic constants, we reproduce the molecular potential energy curves and the spectroscopic levels by following the Rydberg-Klein-Rees procedure [73–76]. This allows us to locate the promising low-energy rovibrational transitions between the two substates of the $X\,^2\Pi$ ground state of the molecules of interest. Such low-energy transitions will exhibit a strong enhancement of sensitivity to VFC. Once the favorable transitions are located, we examine the dependence of their energy on the α and μ constants. Following the line of thought from earlier work [34,40] we derive simple analytical expressions for the transition energies and their fractional variation. Here we do not deal with the lowest vibrational and rotational levels only, but also include the effect of anharmonicity and rotational spacings, which was neglected in earlier publications. Taking only the harmonic frequency ω_e, the first anharmonicity $\omega_e x_e$, the rotational constant B_e, and the spin-orbit coupling constant A_e and its first vibrational dependence $A^{(1)}$ into account (thus neglecting higher order terms), the transition energy ω between the two states can be expressed as

$$\begin{aligned}\omega = (E' - E'')/hc &= \omega_e(v' - v'') - \omega_e x_e(v' - v'')(v'' + v' + 1)\\ &\quad + B_e(J' - J'')(J'' + J' + 1) - A_e - \tfrac{1}{2}A^{(1)}(v'' + v' + 1),\end{aligned} \tag{7}$$

where we denote the initial state by a double prime and the final state by a single prime; in this case these correspond to the $X\,^2\Pi_{3/2}$ and the $X\,^2\Pi_{1/2}$ states, respectively.

The spin-orbit coupling constant A_v and its constituents A_e, $A^{(1)}$, $A^{(2)}$, etc., scale as $\sim\alpha^2$. For the molecules studied here, the rest of the spectroscopic constants are only weakly dependent on α and this dependence can be neglected [40]. Following from the dependence of various spectroscopic constants on the reduced mass [55], we can easily deduce their scaling with the proton-to-electron mass ratio μ: ω_e and $A^{(1)}$ scale as $\sim\mu^{-1/2}$, while $\omega_e x_e$ and B_e scale as $\sim\mu^{-1}$.

Using these analytical dependencies along with Eq. (7), the fractional variation of the transition energy ω can be calculated as

$$\frac{\delta\omega}{\omega} = K_\mu \frac{\delta\mu}{\mu} + K_\alpha \frac{\delta\alpha}{\alpha}, \tag{8}$$

with the relative enhancement factors K_μ and K_α expressed as

$$\begin{aligned}K_\mu = \big[&\tfrac{1}{2}\omega_e(v'' - v') - \omega_e x_e(v'' - v')(v'' + v' + 1)\\ &+ B_e(J'' - J')(J'' + J' + 1)\\ &+ \tfrac{1}{4}A^{(1)}(v'' + v' + 1)\big]\omega^{-1} = \tilde{K}_\mu\omega^{-1},\end{aligned} \tag{9}$$

$$K_\alpha = [-2A_e - A^{(1)}(v'' + v' + 1)]\omega^{-1} = \tilde{K}_\alpha\omega^{-1}, \tag{10}$$

where the symbols $\tilde{K}_\alpha$ and $\tilde{K}_\mu$ represent the absolute enhancement factors.

We have examined the effect of including the next order parameters in the Dunham series, i.e., $\omega_e y_e$, α_e, and $A^{(2)}$, on the calculated K_μ and K_α, and found it to be negligible for the majority of the cases considered here.

IV. RESULTS AND DISCUSSION

We illustrate the scheme outlined above by using $\mathrm{H}^{79}\mathrm{Br}^+$ as an example. Figure 1 presents the reconstructed potential energy curves of the two substates of the $X\,^2\Pi$ ground state of $\mathrm{H}^{79}\mathrm{Br}^+$. We find that the $X\,^2\Pi_{3/2}$, $v = 14$ level is very close in energy to the $X\,^2\Pi_{1/2}$, $v = 12$ level, differing by 19 cm^{-1}. We then take a closer look at the rotational states of the favorable vibrational transition, in order to select even closer quasidegeneracies of the energy levels (Fig. 2, left). Vibrational levels $X\,^2\Pi_{3/2}, v = 15$ and $X\,^2\Pi_{1/2}, v = 13$, albeit further apart (123 cm^{-1}), also exhibit quasidegeneracies in the rotational structure (Fig. 2, right).

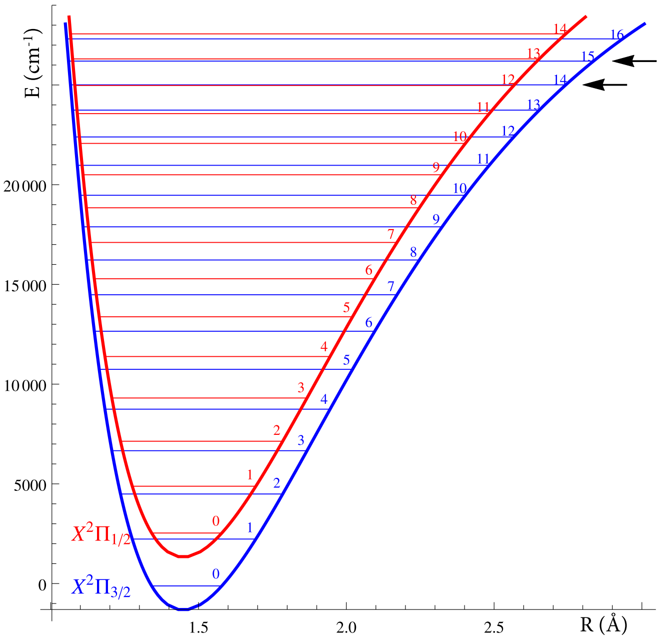

FIG. 1. (Color online) Potential energy curves of the two substates of the $X\,^2\Pi$ state in $\mathrm{H}^{79}\mathrm{Br}^+$. Arrows point to the quasidegenerate vibrational levels. Origin of the vertical axis corresponds to the bottom of the unsplit potential well.

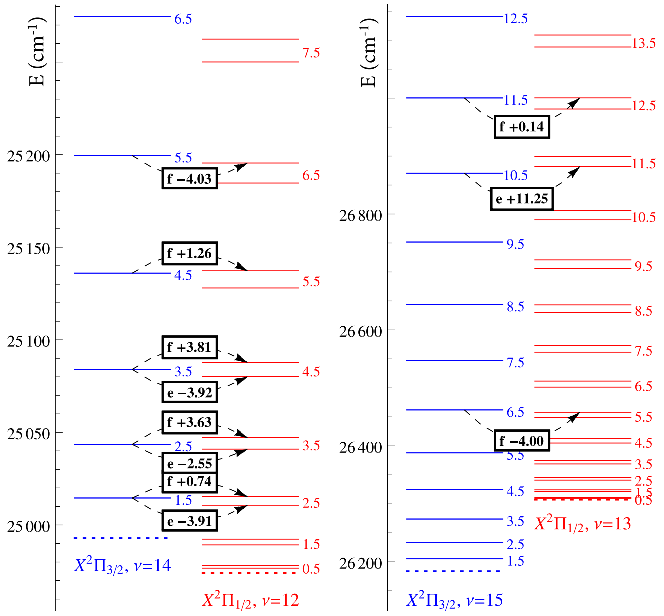

FIG. 2. (Color online) Rotational structure of the selected quasidegenerate vibrational levels of $\mathrm{H}^{79}\mathrm{Br}^+$ with transitions represented by dashed arrows. Allowed $e \leftrightarrow e$ and $f \leftrightarrow f$ transitions are denoted with e and f, respectively, in the text boxes with transition energies (cm^{-1}).

We focus only on the dominant single-photon dipole transitions obeying the $\Delta J = 0, \pm 1$ selection rule. Since the transitions conserving the total angular momentum ($\Delta J = 0$) can be blended together for all values of J [40], thus negatively affecting the accuracy, we are interested in the $\Delta J = \pm 1$ transitions only. Furthermore, we also include the effect of Λ doubling and we only consider transitions following the rotational symmetry selection rule $e \nleftrightarrow f$. The Λ doubling of the $^2\Pi_{3/2}$ rotational levels is negligible and not even visible in the scope of Fig. 2. We can identify a number of rovibrational transitions corresponding to a unit change in the total angular momentum J while having very low transition energies between the reconstructed rovibrational levels. These are listed in Table III, along with the transition energies and the corresponding enhancement factors as defined in Eqs. (9) and (10). The same procedure is performed for the rest of the systems under study. These results are also listed in Table III, and the corresponding plots are presented in the Supplemental Material [77]. Note that there are more favorable transitions identified in the rotational plots, as these usually occur in series for several neighboring rotational levels; however, we only present the ones with lowest ω (and therefore highest K_μ and K_α) in Table III.

The obtained values of K_α look very promising and span orders of magnitude ranging from 10^3 to 10^6. Several transitions in $\mathrm{I}_2{}^+$ and $\mathrm{I}^{81}\mathrm{Br}^+$ are particularly sensitive to variation in α, with K_α values larger than 10^6, due to the almost perfect degeneracy between these levels, differing by only about 0.01 cm^{-1}.

We note that the uncertainties in the experimental data (Table I) translate into uncertainties in the presented values. While these are straightforward and small for the absolute enhancement factors $\tilde{K}_\mu$ and $\tilde{K}_\alpha$ (relative errors are of order of 0.1% for hydrogen halides and of order 1% for dihalogens), the effect on transition energies (appearing in the denominator of relative enhancement factors) is much stronger, as one expects. Positions of the rovibrational energy levels have uncertainties in the order of 1 cm^{-1} for hydrogen halides and in the order of 10 cm^{-1} for dihalogens, much larger than the transitions themselves. However, these uncertainties are coherent for the whole rovibrational spectra and this essentially means "sliding" the rotational levels of the two $X\,^2\Pi$ substates against each other, such that quasidegeneracy occurs at one of the neighboring pairs of rotational levels. Hence, the reported relative enhancements K_μ and K_α should only be considered

TABLE III. Transition energies ω (cm^{-1}) and corresponding enhancement factors, absolute, $\tilde{K}_\mu$ and $\tilde{K}_\alpha$ (cm^{-1}), and relative, K_μ and K_α, for several identified transitions of cations under investigation. Symbols e and f denote the transitions of type $e \leftrightarrow e$ and $f \leftrightarrow f$, respectively.

Cation	v''	v'	J''	J'	s	ω	$\tilde{K}_\mu$	K_μ	$\tilde{K}_\alpha$	K_α
$H^{79}Br^+$	14	12	1.5	2.5	f	0.74	–80.8	–110	5250	7120
			4.5	5.5	f	1.26	–129	–103		4180
	15	13	11.5	12.5	f	0.14	–426	–3030	5250	37 200
$H^{81}Br^+$	14	12	1.5	2.5	f	0.82	–80.4	–97.9	5250	6390
			5.5	6.5	f	−0.27	–145	543		–19 700
	15	13	11.5	12.5	e	−1.44	–426	295	5250	–3630
			6.5	5.5	f	0.52	–119	–228		10 100
$D^{79}Br^+$	9	7	7.5	8.5	f	2.20	881	400	5270	2390
	10	8	1.5	0.5	e	1.99	871	437	5270	2650
$D^{81}Br^+$	9	7	7.5	8.5	f	2.49	881	354	5270	2120
	10	8	1.5	0.5	e	2.23	871	391	5270	2370
HI^+	6	3	3.5	4.5	e	−3.05	2060	–675	10 700	–3490
			21.5	20.5	f	−0.41	2390	–5780		–25 800
	12	8	7.5	8.5	f	1.50	984	656	10 600	7070
			21.5	20.5	e	−2.35	1360	–580		–4510
	16	11	16.5	15.5	e	0.12	190	1630	10 600	91 000
DI^+	7	3	1.5	2.5	e	0.27	2230	8220	10 700	39 300
			21.5	20.5	f	0.98	2390	2420		10 800
			27.5	26.5	e	2.42	2430	1000		4420
	14	9	9.5	10.5	e	−0.91	1460	–1600	10 600	–11 700
			22.5	21.5	f	−0.76	1670	–2190		–14 000
	19	3	9.5	10.5	f	1.08	686	638	10 600	9860
			19.5	18.5	f	−3.64	878	–241		–2910
${I_2}^+$	30	6	30.5	31.5	e	−0.00	2270	–682 000	9990	–3 010 000
			34.5	35.5	f	−0.06	2260	–40 000		–176 000
	39	14	50.5	51.5	e	0.01	2090	230 000	9800	1 080 000
			54.5	55.5	f	−0.13	2090	–16 200		–76 200
	48	22	1.5	2.5	f	0.06	1900	30 500	9610	155 000
			19.5	18.5	e	−0.02	1900	–79 100		–401 000
			28.5	27.5	f	−0.04	1900	–45 900		–232 000
${}^{79}{Br_2}^+$	11	3	22.5	23.5	e	0.15	1350	9170	5570	37 900
			24.5	25.5	f	−0.10	1350	–13 700		–56 600
	31	22	18.5	19.5	e	−0.10	1190	–12 300	5370	–55 400
			21.5	22.5	f	0.04	1190	33 200		150 000
${}^{79,81}{Br_2}^+$	9	1	20.5	21.5	e	0.09	1360	14 500	5600	59 700
			22.5	23.5	f	−0.11	1360	–12 700		–52 200
	30	21	3.5	4.5	e	−0.09	1160	–12 900	5450	–60 400
			4.5	5.5	f	−0.07	1160	–15 500		–73 000
${}^{81}{Br_2}^+$	8	0	12.5	13.5	e	0.11	1370	12 900	5600	52 700
			14.5	15.5	f	0.09	1370	14 500		59 400
	28	19	36.5	37.5	e	0.05	1190	25 700	5450	118 000
			39.5	40.5	f	−0.10	1190	–11 600		–53 400
$I^{79}Br^+$	25	8	30.5	31.5	e	0.14	1720	12 200	9220	65 600
			33.5	34.5	f	0.11	1720	16 300		87 700
	39	22	30.5	31.5	e	−0.20	1020	–5100	9140	–45 500
			33.5	34.5	f	−0.04	1020	–27 900		–249 000
$I^{81}Br^+$	24	7	34.5	35.5	e	0.16	1760	11 200	9320	59 200
			37.5	38.5	f	0.04	1760	45 200		240 000
	36	19	5.5	4.5	f	0.01	1170	216 000	9320	1 720 000
			9.5	8.5	e	0.10	1110	9890		82 700
	37	20	40.5	41.5	e	0.07	1120	15 600	9320	131 000
			43.5	44.5	f	0.11	1170	11 400		90 500
$I^{35}Cl^+$	20	8	19.5	20.5	e	−0.10	1940	–20 100	9550	–98 900
			22.5	23.5	f	−0.21	1940	–9090		–44 800
$I^{37}Cl^+$	20	8	20.5	21.5	e	0.05	1940	42 300	9550	208 000
			23.5	24.5	f	−0.11	1940	–17 300		–85 200

TABLE III. *(Continued.)*

Cation	v''	v'	J''	J'	s	ω	$\tilde{K}_\mu$	K_μ	$\tilde{K}_\alpha$	K_α
IF^+	14	5	26.5	27.5	*e*	−0.56	2760	−4910	11 200	−19 900
			31.5	32.5	*f*	0.27	2760	10 100		40 900
	22	12	40.5	41.5	*e*	0.55	2780	5060	11 100	20 200
			44.5	45.5	*f*	−0.83	2770	2960		11 800
	28	17	40.5	41.5	*e*	−0.81	2820	−3490	11 000	−13 600
			45.5	46.5	*f*	−0.06	2820	−44 600		−173 000

as indications of what one might expect to see in experiment and we stress the importance of high-resolution experimental studies aimed at locating the quasidegeneracies in these ionic systems.

The calculated enhancement factors $\tilde{K}_\mu$ and K_μ are generally one or two orders of magnitude smaller than $\tilde{K}_\alpha$ and K_α, respectively. However, many theories suggest that the variation in μ should be on the order of 30 times larger than that in α (see, e.g., [78], and references therein). Thus, the effect of possible μ variation on the spectra of these systems should not be neglected. Since the first term in Eq. (9) is dominant, we can easily see, that the larger the difference between initial and final state vibrational quantum number v, the higher the enhancement factor K_μ. This is automatically satisfied for heavy diatomics with larger spin-orbit splitting between the two $X\,^2\Pi$ substates as is illustrated by the results in Table III.

The identified transitions in the HBr^+ and HI^+ isotopologues, as well as in $^{79}Br^{81}Br^+$, may be of particular interest for experimental investigation because of their low-J nature. Rotationally cooled molecules should produce spectra with higher resolution [79–82], which is of great importance for detection of the minute changes in transition energies resulting from VFC.

Absolute enhancement factors $\tilde{K}_\alpha$ in molecular ions containing iodine are approximately twice as large as those in ions containing bromine (without iodine) and they roughly follow the expected $\sim Z^2$ scaling.

An advantage can be gained by considering the variation of the ratio of two transition energies within the same rovibronic spectrum, ω_1/ω_2, rather than the variation of the energies themselves [40]. The variation of ω_1/ω_2 is given by

$$\frac{\delta(\omega_1/\omega_2)}{(\omega_1/\omega_2)} = \left(K_\mu^1 - K_\mu^2\right)\frac{\delta\mu}{\mu} + \left(K_\alpha^1 - K_\alpha^2\right)\frac{\delta\alpha}{\alpha}. \tag{11}$$

Considering the variation of a dimensionless ratio of two transition energies removes the dependence on the unit system and minimizes the systematic effects. In addition, selecting two transitions where either K_μ^1 and K_μ^2, or K_α^1 and K_α^2, or both pairs, have an opposite sign, maximizes the sensitivity of the measurement.

V. CONCLUSION

The presented cations of hydrogen halides and dihalogens appear to be promising probes for laboratory measurements of VFC as indicated by the magnitude of the absolute enhancement factors. However, there is an eminent need for more precise spectroscopical studies of these systems in order to be able to predict the relative enhancement factors with confidence. Future investigations in our group will also include negatively charged molecular ions.

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APPENDIX A

Here we briefly define the symbols used in this work, following the definitions and the derivations of Ref. [83]. The energy of a vibrational-rotational level specified by the vibrational quantum number v, the total electronic angular momentum J, and its projection to the internuclear axis Ω ($\Omega = 1/2$ or $\Omega = 3/2$ for a molecule with a $^2\Pi$ ground state) is given by the Dunham series,

$$E_{vJ\Omega}/hc = G_v + F_J \pm \frac{A_v}{2}, \tag{A1}$$

where G_v is the energy of the vibrational level, F_J is the energy of the rotational level, and A_v is the spin-orbit coupling with the positive and the negative signs corresponding to $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states, respectively. The energy of a given vibrational level is defined as a series in $(v + \frac{1}{2})$,

$$\begin{aligned} G_v = {} & \omega_e\left(v + \tfrac{1}{2}\right) - \omega_e x_e\left(v + \tfrac{1}{2}\right)^2 + \omega_e y_e\left(v + \tfrac{1}{2}\right)^3 \\ & + \omega_e z_e\left(v + \tfrac{1}{2}\right)^4 + \cdots . \end{aligned} \tag{A2}$$

Similarly, the energy of a given rotational level is a series in $J(J+1)$,

$$F_J = B_v J(J+1) - D_v J^2(J+1)^2 + \cdots . \tag{A3}$$

The rotational constant B_v and the centrifugal distortion constant D_v depend on the vibrational quantum number v and are given by

$$B_v = B_e - \alpha_e\left(v + \tfrac{1}{2}\right) + \gamma_e\left(v + \tfrac{1}{2}\right)^2 + \epsilon_e\left(v + \tfrac{1}{2}\right)^3 + \cdots , \tag{A4}$$

$$D_v = D_e + \beta_e\left(v + \tfrac{1}{2}\right) + \delta_e\left(v + \tfrac{1}{2}\right)^2 + \cdots . \tag{A5}$$

The vibrationally dependent spin-orbit coupling constant A_v is defined as

$$A_v = A_e + A^{(1)}\left(v + \tfrac{1}{2}\right) + A^{(2)}\left(v + \tfrac{1}{2}\right)^2 + \cdots \tag{A6}$$

and often the centrifugal distortion term $A_{Dv}J(J+1)$ is added to Eq. (A6) as well, with

$$A_{Dv} = A_D + A_D^{(1)}\left(v+\tfrac{1}{2}\right) + A_D^{(2)}\left(v+\tfrac{1}{2}\right)^2 + \cdots. \tag{A7}$$

We note, that an extra term of $-B_v\Omega^2$ (giving rise to an additional energy difference of $2B_v$ between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ substates) ought to be present in the expression for the rotational energy (A3). In practice, however, this term is often effectively absorbed in the spin-orbit splitting (A6). Only in the experimental works on HBr^+ and HI^+ this term was explicitly accounted for in the determination of the spectroscopic constants, hence we also include it only when reconstructing the energy levels of HBr^+ and HI^+.

APPENDIX B

For the sake of completeness we briefly mention the remaining systems belonging to the group of cations of dihalogens and hydrogen halides. ClF^+, BrF^+, and $BrCl^+$ were studied by low-resolution He(I) photoelectron spectroscopy and a few basic spectroscopic constants are given in the corresponding works [84–86]. However, because of the considerable uncertainties in the values, we cannot use these for a detailed analysis. For ClF^+ only the harmonic vibrational frequency $\omega_e = 870 \pm 30$ cm^{-1} and the spin-orbit coupling constant $A_e = -630 \pm 30$ cm^{-1} are reported [84]. Since the value of A_e is smaller than that of ω_e, this renders ClF^+ unfavorable for observing quasidegeneracies between vibrational levels of the $^2\Pi_{3/2}$ and $^2\Pi_{\frac{1}{2}}$ substates. Only with sufficiently large negative $A^{(1)}$ constant, quasi-degeneracy could occur for some higher vibrational levels, but this is unlikely considering the fact that we do not observe this in the related systems ${F_2}^+$ and ${Cl_2}^+$ (discussed below). In the case of BrF^+, three spectroscopic constants are reported, namely, $\omega_e = 750 \pm 30$ cm^{-1}, $\omega_e x_e = 10 \pm 5$ cm^{-1}, and $A_e = -2590 \pm 40$ cm^{-1} [85]. Depending on the value of $A^{(1)}$, this system might exhibit quasidegeneracies similar to the IF^+ cation, but we cannot draw any further conclusions from the present values. The $BrCl^+$ cation seems to be the most promising of these three systems with the reported values $\omega_e = 498 \pm 20$ cm^{-1}, $\omega_e x_e = 2.5 \pm 5.0$ cm^{-1}, $A_e = -2070 \pm 30$ cm^{-1}, and $A^{(1)} = -24 \pm 20$ cm^{-1} [86]. Since the spin-orbit coupling constant is approximately four times the harmonic vibrational frequency, there is a possibility of quasidegeneracy between the $^2\Pi_{3/2}(v=4)$ and $^2\Pi_{1/2}(v=0)$ levels. The energies corresponding to these levels (with respect to the bottom of the $^2\Pi_{3/2}$ potential well) are 2140 ± 160 cm^{-1} and 2320 ± 40 cm^{-1}, respectively, showing a slight overlap between the two uncertainty intervals. A similar situation holds for several higher vibrational levels.

The HF^+, HCl^+, and ${F_2}^+$ cations were studied extensively by experiment and their spectroscopic constants are known to high precision. However, since the spin-orbit coupling constant is much smaller than the vibrational frequency ($A_e = -292.6$ cm^{-1}, $\omega_e = 3097.1$ cm^{-1} for HF^+ [87], $A_e = -648.3$ cm^{-1}, $\omega_e = 2673.7$ cm^{-1} for $H^{35}Cl^+$ [88], and $A_e = -337$ cm^{-1}, $\omega_e = 1089.4$ cm^{-1} for ${F_2}^+$ [89]), no quasidegeneracy between the $X\,^2\Pi$ substates is observed throughout the whole region of vibrational levels. A similar situation holds for the deuterated species DF^+ and DCl^+. This is nicely illustrated for all three cations in the spectra in Refs. [90–92].

Although ${Cl_2}^+$ was previously suggested as a good candidate for VFC study [93] based on spectroscopic constants from Ref. [94], recent data from high-resolution spectroscopy [95] revealed that the match between the spin-orbit coupling constant and the vibrational frequency is not as fortuitous as expected. The corresponding values from this study are $A_e = -717.5$ cm^{-1} and $\omega_e = 645.6$ cm^{-1} for $^{35}{Cl_2}^+$. Since the $^2\Pi_{g,1/2}(v=0)$ level is above the $^2\Pi_{g,3/2}(v=1)$ level, and the vibrational dependence of the spin-orbit term A_v is negligible, every subsequent pair of levels is even further apart in energy because of the effect of anharmonicity. The smallest energy difference of 59.5 cm^{-1} between levels $X\,^2\Pi_{g,1/2}$, $v=0$ and $X\,^2\Pi_{g,3/2}$, $v=1$ can be observed for the $^{37}{Cl_2}^+$ isotopologue; however, this is still too large. The value of the rotational constant B_e is approximately 0.28 cm^{-1}, hence no further improvement can be obtained for any rotational levels. Nevertheless, the ${Cl_2}^+$ is still an interesting system with many quasidegeneracies between the vibrational levels of the ground state $X\,^2\Pi_g$ and excited states $A\,^2\Pi_u$, $B\,^2\Delta_u$, and $a\,^4\Sigma_u^-$, which we investigate in a separate study.

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