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Complete characterization of the $3p$ Rydberg complex of a molecular ion: MgAr^+

II. Global analysis of the $\text{A}^+ \ ^2\Pi$ and $\text{B}^+ \ ^2\Sigma^+ (3p_{\sigma,\pi})$ states

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We report a global study of the $3p$ Rydberg complex of the MgAr^+ molecular ion. High-resolution spectroscopic data on the two spin-orbit components of the A^+ electronic state were obtained by isolated-core multiphoton Rydberg-dissociation spectroscopy up to vibrational levels as high as $v' = 29$, covering more than 90% of the potential wells. Accurate adiabatic potential-energy functions of the A^+ and B^+ states, which together form the $3p$ Rydberg complex, were obtained in a global direct-potential-fit analysis of the present data and the extensive data on the B^+ state reported in the companion article. The dissociation energies of the B^+ state, the two spin-orbit components of the A^+ state and the X^+ state of MgAr^+ are obtained with uncertainties (1 cm^{-1}) more than two orders of magnitude smaller than in previous studies.

I. INTRODUCTION

The complete experimental characterization of molecular Rydberg states necessitates the measurement of spectra of a large number of states of different principal and angular-momentum quantum numbers and, for each of them, of a large number of rotational and vibrational levels, extending from the vibrational ground state to levels close to the dissociation threshold^{1–10}. This task is particularly difficult for cations because of the low densities in which they can be produced compared to neutral species and the larger photon energies required for electronic excitation. In addition, diatomic cations produced by conventional ion sources are in most cases in their vibrational ground state, which restricts the accessible vibrational levels of electronically-excited states to those having significant Franck-Condon overlap with the ground vibronic state. For this reason, hardly any systematic studies of the Rydberg states of molecular cations have been reported so far. This situation is in stark contrast to that prevailing for the ground and low-lying valence states of cations, for which many examples of detailed characterization by high-resolution spectroscopy are known, see, *e.g.*, Refs. 11–20 and references therein.

We showed recently, with the example of MgAr^+ , that *state-selected* cations can be prepared in a wide range of vibrational levels of the electronic ground state by photoexcitation of neutral molecules to high-lying Rydberg states²¹. For sufficiently large values of the principal quantum number ($n \geq 100$) or orbital-angular-momentum quantum number of the Rydberg electron, the ionic core of the Rydberg molecule can be considered as *isolated* from the Rydberg electron, and behaves as the bare ion. With the method of isolated-core multiphoton Rydberg-dissociation (ICMRD) spectroscopy²¹, the ionic core is first prepared in a selected vibrational level of

the electronic ground state and subsequently photodissociated in a multiphoton process. ICMRD spectroscopy opens up the possibility of systematically studying a broad range of vibrational levels belonging to electronically excited states of molecular ions in a background-free manner. As a demonstration, we have recorded spectra of the $3p_{\sigma} \text{B}^+(v')$ state of MgAr^+ starting from the ground vibrational level ($v' = 0$) and extending to the dissociation limit and beyond²². The present article extends this study to the $3p_{\pi}$ component, which consists of the two $\Omega = 1/2$ and $\Omega = 3/2$ spin-orbit components of the A^+ state.

The four lowest electronic states of MgAr^+ follow the structure of the $3s$ and $3p$ orbitals of the Mg^+ ion, and thus possess a Rydberg character in the sense of Mulliken²³ (see Fig. 2 in Ref. 22). The $3s_{\sigma} \text{X}^+ \ ^2\Sigma^+$ ground state correlates to the $\text{Ar}(^1S_0) + \text{Mg}^+(^2S_{1/2})$ dissociation asymptote, whereas the $3p$ complex consists of three excited electronic states correlating to the $\text{Ar}(^1S_0) + \text{Mg}^+(^2P_{1/2,3/2})$ dissociation limits. At short internuclear distances, two of these states can be regarded as the two spin-orbit components of the $3p_{\pi} \text{A}^+ \ ^2\Pi_{\Omega'=1/2,3/2}$ state, and the third as the $3p_{\sigma} \text{B}^+ \ ^2\Sigma^+$ state. They will be denoted as $\text{A}^+_{1/2}$, $\text{A}^+_{3/2}$ and B^+ below. The low-lying vibrational levels ($v' \leq 14$) of the two spin-orbit components of the A^+ state were first observed in the pioneering work of Duncan and co-workers^{24–26}, and the rotational constant of the $v' = 5$ state was determined in a subsequent high-resolution study²⁷. Spectra of the $\text{A}^+(v' = 0, 1, 5) \leftarrow \text{X}^+(v'' = 3)$ vibrational bands with a partially resolved rotational structure were also observed recently by ICMRD spectroscopy²¹. In parallel, the A^+ state of MgAr^+ was investigated theoretically in Refs. 22,28–35. The rovibrational structure of the B^+ state has first been measured in the study reported in the companion paper²².

The present article reports high-resolution spectroscopic data on the A^+ state of MgAr^+ obtained by ICMRD spectroscopy. Vibrational levels as high as $v' = 29$ have been observed and the rotational structure of the vibrational bands could be partially resolved

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up to $v' = 28$. The data cover more than 90% the potential wells of each of the two spin-orbit components of the A^+ state. Combined with the data reported on the B^+ state in the companion paper²², which cover its entire potential depth, the new data provide complete and detailed information on the $3p$ Rydberg complex of $MgAr^+$. From the experimental results, high-accuracy adiabatic potential-energy functions were determined for the three electronic states using a direct-potential-fit technique³⁶ combined with a model describing the spin-orbit interaction at the relevant internuclear distances. A similar approach was previously used to describe the ground and first electronically excited states of the homonuclear rare-gas dimers^{37–41}.

II. EXPERIMENT

The experimental setup and the technique of ICMRD spectroscopy used in the present work were described in detail in Refs. 21,42. Briefly, a molecular beam containing rotationally and vibrationally cold $MgAr$ molecules is first formed in a pulsed laser-ablation supersonic-expansion source. $MgAr$ molecules are, for their vast majority, in the metastable $Mg(3s3p)Ar$ a $^3\Pi_0(v=0)$ state and their rotational temperature is estimated to be of the order of 10 K for the data presented below. After passing through a 3-mm-diameter skimmer located 8 cm downstream from the source, the molecular beam enters the photoexcitation chamber, where it is intersected at right angles by the beams of two pulsed dye lasers pumped by the second harmonic of a Nd:YAG laser.

The first laser pulse, corresponding to the frequency-tripled output of the first dye laser and with a wave number tunable in the range from 39000 cm^{-1} to 39500 cm^{-1} , excites the neutral $MgAr$ molecules from the metastable a $^3\Pi_0$ state to high-lying Rydberg states with principal quantum numbers $n \simeq 120$ lying just below a specific $X^+ \ ^2\Sigma^+(v'')$ ionization threshold of $MgAr$. The second laser pulse, corresponding to the frequency-doubled output of the second dye laser and with a wave number $\tilde{\nu}_2$ tunable in the range from 31000 cm^{-1} to 35800 cm^{-1} , resonantly excites the ionic core from the selected $X^+(v'')$ state to a vibrational level (v') of either of the two spin-orbit components of the A^+ excited state. Further photoabsorption leads to the dissociation of the molecule into a ground-state neutral Ar atom and a Mg atom in a high Rydberg state²¹.

The interaction between the $MgAr$ molecules and the laser pulses occurs within a 5.8-cm-long stack of five equally spaced and resistively coupled cylindrical electrodes. A small electric field of $\simeq 1.7\text{ V/cm}$ is applied across the stack immediately after photoexcitation and photodissociation, and displaces the ions produced by the laser pulses, called prompt ions, away from the interaction region without affecting the atoms and molecules excited to Rydberg states. After $\simeq 5\text{ }\mu\text{s}$, a pulsed extraction field of 130 V/cm is applied to the stack to field

ionize the Rydberg atoms and molecules and accelerate all positively-charged particles into a linear time-of-flight region, at the end of which they are detected by a micro-channel-plate detector. The spatial separation between the prompt and pulsed-field-ionized ions prior to extraction makes it possible to distinguish them by their time of flight. By recording the yield of Mg^+ ions produced by delayed pulsed field ionization as a function of the wave number of the second laser, the resonance-enhanced multiphoton dissociation of the $MgAr^+$ ion core *via* the A^+ state can be recorded in a background-free manner.

III. EXPERIMENTAL RESULTS

We have recorded the spectra of the transitions from the $X^+(v'')$ to the $A_{\Omega'}^+(v')$ states of $^{24}MgAr^+$ with $\Omega' = 1/2$ and $3/2$ and $v' = 0 - 29$. For each v' , the value of the vibrational quantum number v'' of the initial state was chosen so that the corresponding Franck-Condon factor was large enough for the transition to be observed. The assignment of the observed bands to given values of v' and v'' is based on the isotopic-shift analysis carried out in previous studies^{21,25,43}. The ability to prepare the ground-state molecular ion in a broad range of selected (ro)vibrational states ($v'' = 0 - 9$ in the present case) is a property of the isolated-core multiphoton Rydberg-dissociation technique and is essential for observing vibrational states of the A^+ excited electronic state with v' as high as 29. In contrast, ion-beam-based techniques are typically limited to the rotational and vibrational levels of the ground electronic state of the ion that are thermally populated in the ion source, *e.g.*, $v'' = 0 - 1$ in the case of $MgAr^+$ ^{24,25}, which limits the accessible vibrational levels of the A^+ state to $v' \leq 14$ ^{24,25}.

Figures 1 and 2 show high-resolution spectra of the $A_{1/2}^+(v' = 17) \leftarrow X^+(v'' = 3)$ and $A_{3/2}^+(v' = 17) \leftarrow X^+(v'' = 3)$ bands, respectively. Their rotational structure consists of four branches associated with transitions from the rotational levels of the $X^+ (^2\Sigma^+)$ state, described by Hund's coupling case (b) and labeled by the quantum number N'' associated with the total angular momentum without spin, to rotational levels of the $A^+ (^2\Pi_{\Omega'})$ states, described by Hund's coupling case (a) and labeled by the quantum number J' associated with the total angular momentum. In the case of the transition to the $A_{1/2}^+(v' = 17)$ level, shown in Fig. 1, the rotational structure is fully resolved except in the region of the bandhead of the $\Delta_{J',N''} = J' - N'' = -0.5$ branch between 34779.9 cm^{-1} and 34781.5 cm^{-1} . As in our previous work²¹, the positions of these individual lines were determined by fitting them with Gaussian functions with a full width at half maximum of 0.1 cm^{-1} . The origin of the band $\tilde{\nu}_{v',v''}$ and the rotational constants $B_{v''}''$ and $B_{v'}'$ of the initial and final states, respectively, were obtained from the line positions in a least-squares fit based on the

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Figure 1. Measured and calculated spectra of the $A_{1/2}^+(v' = 17) \leftarrow X^+(v'' = 3)$ band of $^{24}\text{MgAr}^+$. The assignment bars give the positions of the transitions to levels of the A^+ state of successive values of J' . The red arrow indicates the position of the $A_{1/2}^+(v' = 17, J' = 1/2) \leftarrow X^+(v'' = 3, N'' = 2)$ transition.

Figure 2. Measured and calculated spectra of the $A_{3/2}^+(v' = 17) \leftarrow X^+(v'' = 3)$ band of $^{24}\text{MgAr}^+$. The assignment bars give the positions of the transitions to levels of the A^+ state of successive values of J' . The red arrow indicates the calculated position of the hypothetical transition $A_{3/2}^+(v' = 17, J' = 1/2) \leftarrow X^+(v'' = 3, N'' = 2)$. This transition is not observed, indicating that $\Omega' = 3/2$.

standard expression^{44,45}

$$\tilde{\nu} = \tilde{\nu}_{v',v''} + B_{v'}' [J'(J' + 1) - \Omega'^2] - B_{v''}'' N''(N'' + 1). \quad (1)$$

At the low values of N'' and J' relevant in the present experiment ($N'' \lesssim 11$, $J' \lesssim 25/2$), the effects of the centrifugal distortion on the positions of the rotational levels are negligible.

The 1σ statistical uncertainties of the band origins determined in the fit are $\Delta\tilde{\nu}_{v',v''} = 0.1 \text{ cm}^{-1}$. They represent the standard deviation of values extracted from several independent spectra recorded under identical experimental conditions²¹. The systematic uncertainties of the band origins are 0.04 cm^{-1} and correspond to the absolute accuracy of the wave-number calibration. The 1σ statistical uncertainties of the rotational constants are those resulting from the least-squares fits. The spectra displayed in the lower panel of Figs. 1 and 2 were calculated using the fit results and the rotational line strengths for transitions from a state described by Hund's coupling case (b) to a state described by Hund's coupling case (a)⁴⁵. The initial rotational states were assumed to be thermally populated at a temperature of 7 K. The agreement between the experimental and simulated spectra is excellent, with the exception of the intensities of the members of the $\Delta J'N'' = -1.5$ branch, which appear underestimated in the simulation. Possible reasons for this discrepancy are discussed in Ref. 21.

The assignment of the bands to particular values of v' and v'' is known^{21,25,43}. However, their attribution to $\Omega' = 1/2$ or $\Omega' = 3/2$ relied until now on the assumption that the energetic ordering of the two spin-orbit components of the A^+ molecular state is regular, as in the case of the $3p_j$ ($j = 1/2, 3/2$) states of Mg^+ , and therefore that the levels with $\Omega' = 1/2$ are lower in energy than the corresponding ones with $\Omega' = 3/2$ ²⁷. The spectra of the $A_{1/2}^+(v' = 17) \leftarrow X^+(v'' = 3)$ and $A_{3/2}^+(v' = 17) \leftarrow X^+(v'' = 3)$ bands shown in Figs. 1 and 2 unambiguously verify this assumption. For $\Omega' = 1/2$, the lowest possible value of J' is $1/2$ and the line corresponding to the transition from $N'' = 2$ to $J' = 1/2$, marked by a red arrow in Fig. 1, confirms that the final electronic state of the transition is indeed an $\Omega' = 1/2$ state. For $\Omega' = 3/2$, $J' \geq 3/2$ and the transition from $N'' = 2$ to $J' = 1/2$ cannot be observed. The wave number at which one would expect such a transition for an $\Omega' = 1/2$ final state was calculated using Eq. (1), and is marked by the red arrow in Fig. 2. The absence of a line at this position in the experimental spectrum confirms the attribution to the $\Omega' = 3/2$ final state.

The band origins $\tilde{\nu}_{v',v''}$ determined from least-squares fits of the experimental spectra recorded from the X^+ ground-state levels with $v'' = 3, 6, 7$ and 9 to A^+ levels up to $v' = 29$ are listed in Table I, along with the rotational constants of the $A_{1/2,3/2}^+(v')$ states up to $v' = 28$. In some cases, only a few isolated rotational lines could be identified. To increase the reliability of the fit results, $B_{v''}''$ was fixed to the weighted average of the values determined from other bands (see Table II). The 1σ statis-

tical uncertainty of $B'_{v'}$ was also increased to 0.01 cm^{-1} in these cases. In the case of $v' = 29$, only prominent bandheads were observed, which did not permit the determination of B'_{29} for either of the two spin-orbit components. The band origins were obtained in least-squares fits of the simulated rotational contours of the bands to the experimental spectra after fixing the values of B'_{29} to the values (0.099 cm^{-1} for both $\Omega' = 1/2$ and $3/2$) obtained by extrapolation using the standard expression⁴⁴ is twice as large as the uncertainties of the other band origins.

$$B'_{v'} = B_e - \alpha_e \left(v' + \frac{1}{2} \right) + \beta_e \left(v' + \frac{1}{2} \right)^2. \quad (2)$$

Table I: Observed band origins $\tilde{\nu}_{v'v''}$ of the $A_{\Omega'}^+(v') \leftarrow X^+(v'')$ transitions. The term values $T_{v'}'^{(\text{obs})}$ of the $A_{\Omega'}^+(v')$ levels are also given, along with the difference between these values and those extracted from available experimental data^{25,27} ($\Delta T_{v'}'^{(1)}$) and those calculated using the potential-energy functions determined in this article ($\Delta T_{v'}'^{(2)} = T_{v'}'^{(\text{obs})} - T_{v'}'^{(\text{calc})}$). The measured rotational constants $B_{v'}'^{(\text{obs})}$ of the $A_{\Omega'}^+(v')$ levels are also compared to the results obtained from these potential-energy functions ($\Delta B_{v'}' = B_{v'}'^{(\text{obs})} - B_{v'}'^{(\text{calc})}$). All values are in cm^{-1} . The values in parentheses represent one standard deviation in units of the last digit.

v'	Ω'	v''	$\tilde{\nu}_{v'v''}$	$T_{v'}'^{(\text{obs})}$	$\Delta T_{v'}'^{(1)}$	$\Delta T_{v'}'^{(2)}$	$B_{v'}'^{(\text{obs})}$	$\Delta B_{v'}'$
0	1/2	3	31 153.72(10)	—	—	—	0.1950(30)	0.0001
0	3/2	3	31 230.71(10)	76.99(14)	1.09	0.16	0.1920(40)	−0.0026
1	1/2	3	31 419.76(10)	266.04(14)	−1.06	0.08	0.1900(10)	−0.0024
1	3/2	3	31 496.07(10)	342.35(14)	−1.95	0.03	0.1910(20)	−0.0011
2	1/2	3	31 679.25(10)	525.53(14)	0.13	0.02	0.1899(7)	0.0001
2	3/2	3	31 755.17(10)	601.45(14)	1.35	0.05	0.1900(20)	0.0005
3	1/2	3	31 932.39(10)	778.67(14)	0.67	0.03	0.1890(20)	0.0018
3	3/2	3	32 007.78(10)	854.06(14)	0.16	−0.01	0.1890(10)	0.0021
4	1/2	3	32 179.12(10)	1025.40(14)	2.20	0.08	0.1841(8)	−0.0005
4	3/2	3	32 254.03(10)	1100.31(14)	1.31	0.02	0.1837(2)	−0.0005
5	1/2	3	32 419.32(10)	1265.60(14)	6.20	0.08	0.1813(2)	−0.0006
5	3/2	3	32 493.79(10)	1340.07(14)	3.67	0.04	0.1818(2)	0.0002
6	1/2	3	32 653.05(10)	1499.33(14)	6.73	0.13	0.1800(30)	0.0008
6	3/2	3	32 727.04(10)	1573.32(14)	6.62	0.07	0.1790(20)	0.0002
7	1/2	3	32 880.17(10)	1726.45(14)	5.15	0.12	0.1750(10)	−0.0014
7	3/2	3	32 953.68(10)	1799.96(14)	4.86	0.03	0.1760(20)	−0.0001
8	1/2	3	33 100.66(10)	1946.94(14)	4.54	0.09	0.1730(20)	−0.0006
8	3/2	3	33 173.62(10)	2019.90(14)	5.30	−0.10	0.1743(10)	0.0010
9	1/2	3	33 314.54(10)	2160.82(14)	6.42	0.09	0.1695(10)	−0.0012
9	3/2	3	33 387.06(10)	2233.34(14)	5.84	−0.10	0.1717(10)	0.0013
10	1/2	3	33 521.58(10)	2367.86(14)	6.86	−0.05	0.1684(10)	0.0006
10	3/2	3	33 593.81(10)	2440.09(14)	6.49	−0.09	0.1684(10)	0.0009
11	1/2	3	33 722.03(10)	2568.31(14)	6.61	−0.04	0.1653(10)	0.0004
11	3/2	3	33 793.78(10)	2640.06(14)	6.26	−0.12	0.1653(6)	0.0007
12	1/2	7	33 602.61(10)	2761.97(20)	6.87	−0.03	0.1637(5)	0.0019
12	3/2	7	33 673.92(10)	2833.28(20)	6.68	−0.11	0.1630(10)	0.0015
13	1/2	7	33 789.43(10)	2948.79(20)	6.59	−0.01	0.1562(8)	−0.0025
13	3/2	7	33 860.29(10)	3019.65(20)	7.95	−0.11	0.1582(2)	−0.0002
14	1/2	7	33 969.32(10)	3128.68(20)	4.48	−0.04	0.1540(20)	−0.0016
14	3/2	7	34 039.72(10)	3199.08(20)	6.08	−0.17	0.1570(30)	0.0017

Table I – continued from previous page

v'	Ω'	v''	$\tilde{\nu}_{v'v''}$	$T_{v'}^{(\text{obs})}$	$\Delta T_{v'}^{(1)}$	$\Delta T_{v'}^{(2)}$	$B_{v'}^{(\text{obs})}$	$\Delta B_{v'}$
15	1/2	3	34 455.40(10)	3301.68(14)	–	–0.01	0.1519(7)	–0.0005
15	3/2	3	34 525.47(10)	3371.75(14)	–	–0.05	0.1530(8)	0.0010
16	1/2	3	34 621.38(10)	3467.66(14)	–	–0.02	0.1491(7)	0.0001
16	3/2	3	34 691.06(10)	3537.34(14)	–	–0.04	0.1492(5)	0.0005
17	1/2	3	34 780.38(10)	3626.66(14)	–	0.02	0.1455(2)	–0.0002
17	3/2	3	34 849.64(10)	3695.92(14)	–	–0.02	0.1448(4)	–0.0006
18	1/2	3	34 932.30(10)	3778.58(14)	–	0.03	0.1417(2)	–0.0005
18	3/2	3	35 001.21(10)	3847.49(14)	–	0.04	0.1420(4)	0.0001
19	1/2	3	35 077.15(10)	3923.43(14)	–	0.07	0.1376(10)	–0.0010
19	3/2	3	35 145.69(10)	3991.97(14)	–	0.09	0.1380(5)	–0.0003
20	1/2	7	34 901.78(10)	4061.14(20)	–	0.08	0.1362(4)	0.0012
20	3/2	7	34 969.91(10)	4129.27(20)	–	0.06	0.1348(2)	0.0001
21	1/2	7	35 032.34(10)	4191.70(20)	–	0.06	0.1327(3)	0.0014
21	3/2	7	35 100.24(10)	4259.60(20)	–	0.16	0.1302(10)	–0.0008
22	1/2	6	35 227.25(10)	4315.20(24)	–	0.12	0.1273(5)	–0.0001
22	3/2	6	35 294.82(10)	4382.77(24)	–	0.21	0.1280(10)	0.0008
23	1/2	6	35 343.73(10)	4431.67(24)	–	0.28	0.1237(10)	0.0002
23	3/2	6	35 410.79(10)	4498.74(24)	–	0.16	0.1239(10)	0.0007
24	1/2	6	35 452.75(10)	4540.70(24)	–	0.10	0.1195(4)	0.0000
24	3/2	6	35 519.78(10)	4607.72(24)	–	0.18	0.1191(5)	–0.0001
25	1/2	6	35 554.84(10)	4642.79(24)	–	0.05	0.1161(10)	0.0008
25	3/2	6	35 621.67(10)	4709.61(24)	–	0.15	0.1154(4)	0.0003
26	1/2	7	35 578.56(10)	4737.92(20)	–	0.07	0.1096(10)	–0.0015
26	3/2	7	35 645.15(10)	4804.51(20)	–	0.08	0.1097(2)	–0.0012
27	1/2	9	35 536.79(10)	4825.82(24)	–	–0.17	0.1080(8)	0.0013
27	3/2	9	35 603.45(10)	4892.48(24)	–	–0.03	0.1080(20)	0.0014
28	1/2	9	35 617.88(10)	4906.91(24)	–	–0.32	0.1040(10)	0.0018
28	3/2	9	35 684.62(10)	4973.65(24)	–	–0.16	0.1050(10)	0.0028
29	1/2	9	35 691.99(20)	4981.02(30)	–	–0.63	–	–
29	3/2	9	35 759.01(20)	5048.04(30)	–	–0.43	–	–

To obtain the vibrational term values of the observed A^+ levels we first determined the difference in energy $T_{v''}'' - T_3''$ between the various vibrational levels of the initial X^+ state used to record the spectra ($v'' = 6, 7, 9$) and the $v'' = 3$ level. For that purpose we recorded spectra of transitions from at least two different initial levels v'' to the same final level v' and determined the corresponding ground-state combination differences, reported in Table II along with the respective rotational constants $B_{v''}''$. The present values of the energy differences agree within the error bars with those determined from the PFI-ZEKE photoelectron spectrum of the $X^+ \leftarrow a^3\Pi_0$ photoionization transition⁴³. The values of the rotational constants $B_{v''}''$ of the X^+ vibrational states were obtained as weighted averages of the values determined in the fits of individual bands. The present

values for $B_{v''}''$ are in good agreement with the values derived from the potential-energy function of the X^+ state reported in Ref. 43.

Using the energy differences $T_{v''}'' - T_3''$ discussed above, the term values of the levels of the A^+ state are obtained from the band origins $\tilde{\nu}_{v'v''}$ using

$$T_{v'}' = \tilde{\nu}_{v'v''} + (T_{v''}'' - T_3'') - \tilde{\nu}_{03}, \quad (3)$$

as listed in Table I, where they are compared with the values reported by Pilgrim *et al.*²⁵. The two sets of term values differ by up to $\sim 6 \text{ cm}^{-1}$, and the differences increase with v' .

Table II. Rotational constants $B''_{v''}$ of the $X^+(v'')$ states and observed combination differences $T''_{v''} - T''_3$ with respect to the $v'' = 3$ vibrational level, determined from the band origins $\tilde{\nu}_{v'v''}$ of $A^+_{{\Omega'}'}(v') \leftarrow X^+(v'')$ transitions. All values are in cm^{-1} . The values in parentheses represent one standard deviation in units of the last digit.

v''	v'	Ω'	$\tilde{\nu}_{v'v''}$	$T''_{v''} - T''_3$
3	11	3/2	33 793.78(10)	
7	11	3/2	33 480.70(10)	313.08(14)
7	25	3/2	35 550.25(10)	
6	25	3/2	35 621.68(10)	241.67(20)
7	21	1/2	35 032.34(10)	
9	21	1/2	34 902.67(10)	442.75(20)
v''			$B''_{v''}$	$B''_{v''}{}^{43}$
3			0.127 27(9)	0.128
6			0.116 33(30)	0.116
7			0.111 32(11)	0.112
9			0.106 01(30)	0.103

IV. MODEL POTENTIALS

The present data for the A^+ state of MgAr^+ extend up to $v' = 29$ and cover more than 90% of the total depth of the interaction potentials. Combined with the data reported for the B^+ state²², which extend from the vibrational ground state to the dissociation limit, they provide a complete and detailed picture of the $(3p_\sigma, 3p_\pi)$ Rydberg complex of MgAr^+ and can be used to derive accurate adiabatic potential-energy functions describing the three electronic states associated with the $3p$ complex in a global fit. For that purpose, the treatment of the spin-orbit interaction between the three states is necessary.

At large internuclear distances, the three states of the $3p$ complex converge to the two $\text{Mg}^+(3p_{1/2,3/2}) + \text{Ar}(^1S_0)$ dissociation limits (see Fig. 4 in Sec. V below). In this region, the spin-orbit interaction dominates over other interactions and the states are well described by Hund's angular-momentum-coupling case (c). They are labeled by an index specifying their dissociation limit (II for $\text{Mg}^+(3p_{1/2})$ and III for $\text{Mg}^+(3p_{3/2})$), and by Ω' , the quantum number corresponding to the projection of the total electronic angular momentum onto the internuclear axis. This nomenclature yields the symbols II(1/2), III(1/2) and III(3/2) for the three electronic states of the $3p$ complex. At shorter internuclear distances, the spin-orbit interaction becomes weaker than electrostatic interactions so that the quantum numbers Λ and Σ associated with the projections of the orbital and spin angular momenta onto the internuclear axis become good quantum numbers. The three electronic states are well described by Hund's coupling cases (a) and (b), and are designated $A^+ {}^2\Pi_{1/2}$, $A^+ {}^2\Pi_{3/2}$ and $B^+ {}^2\Sigma^+$ respectively. The different symbols associated with the three states of the $3p$ complex at different internuclear distances R and their connection to the nomenclature $A^+_{1/2}$, $A^+_{3/2}$, B^+ used in

Figure 3. Measured spectra of the $B^+(v' = 1) \leftarrow X^+(v'' = 7)$ (top) and $B^+(v' = 14) \leftarrow X^+(v'' = 7)$ (bottom) bands of $^{24}\text{MgAr}^+$. The assignment bars give the positions of the transitions to levels of the B^+ state of successive values of either N' for $v' = 1$, described by Hund's coupling case (b), or J' for $v' = 14$, described by Hund's coupling case (c).

State	Small R	Large R
$A_{1/2}^+$	${}^2\Pi_{1/2}$	$\Pi(1/2)$
$A_{3/2}^+$	${}^2\Pi_{3/2}$	$\text{III}(3/2)$
B^+	${}^2\Sigma^+$	$\text{III}(1/2)$

Table III. Summary of the various denominations of the three electronic states of the $3p$ complex of MgAr^+ in dependence of the internuclear distance R .

this article are summarized in Table III.

A transition between Hund's coupling cases (a) or (b) and Hund's coupling case (c) takes place as the internuclear distance increases and results in a progressive mixing of the ${}^2\Sigma$ and ${}^2\Pi$ characters of the states with $\Omega' = 1/2$, caused by the increasing importance of the spin-orbit interaction. The $\Omega' = 3/2$ state remains unaffected and retains its ${}^2\Pi_{3/2}$ Hund's case (a) character at large R values. Consequently, in order to obtain the adiabatic potential-energy functions of all three electronic states at all internuclear distances R , a correct description of the evolution of the spin-orbit coupling with R is required.

Because the $3p$ complex of MgAr^+ is well isolated from other electronic states, the potential-energy functions can be described reliably using a model originally developed by Cohen and Schneider⁴⁷. This model was used, for example, to study the transition from Hund's coupling case (a) to (c) in the electronic states of the $6p$ complex in Au-rare gases dimers⁴⁸ and in the low-lying electronic states of the rare-gas dimer ions^{37–41}. In the latter case, it is necessary to further take into account the R dependence of the spin-orbit coupling constant^{40,41}. In the model, the spin-orbit interaction can be written, within the adiabatic approximation and using Hund's coupling case (a) basis functions, in the following matrix form:

$$\begin{pmatrix} V_{\Sigma}(R) & \frac{a(R)}{\sqrt{2}} & 0 \\ \frac{a(R)}{\sqrt{2}} & V_{\Pi}(R) - \frac{a(R)}{2} & 0 \\ 0 & 0 & V_{\Pi}(R) + \frac{a(R)}{2} \end{pmatrix}. \quad (4)$$

The eigenvalues of this matrix are the adiabatic potential-energy curves of the three electronic states ($\Pi(1/2)$, $\text{III}(1/2)$ and $\text{III}(3/2)$) of the $3p$ complex. $a(R)$ is the (positive) spin-orbit constant and $V_{\Sigma}(R)$ and $V_{\Pi}(R)$ are the potential-energy functions of the electronic states without spin-orbit interaction. Along the matrix diagonal, one recognizes the potential-energy functions of the ${}^2\Sigma^+$, ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ states, respectively, the latter two being split by the spin-orbit interaction $a(R)$. The off-diagonal matrix elements couple the two states with $\Omega' = 1/2$ and are responsible for the transition to Hund's coupling case (c) at large internuclear distances, where the potential energies V_{Σ} and V_{Π} are almost degenerate. Consequently, the electronic states $\Pi(1/2)$ and $\text{III}(1/2)$ possess mixed Σ and Π character, as discussed above. In the separated-atom limit, the splitting between the

$\Pi(1/2)$ and $\text{III}(1/2, 3/2)$ states predicted by the model is $\frac{3}{2}a(R)$, and must be equal to the $3p_{1/2} - 3p_{3/2}$ spin-orbit splitting of Mg^+ (91.57 cm^{-149}), which implies that $a(R \rightarrow \infty) = 61.05 \text{ cm}^{-1}$. The R -dependence of $a(R)$ is *a priori* unknown. However, it was found to be well described by Morse-type functions in previous studies of the rare-gas-dimer ions^{40,41}. The functional form for $a(R)$ used in the present study is described below.

In the case of the B^+ state, the transition from Hund's coupling case (b) to Hund's coupling case (c) is directly visible in the high-resolution spectra of the $B^+(v') \leftarrow X^+(v'' = 7)$ transitions recorded for increasing v'^{22} . The $v' = 1$ and $v' = 14$ bands are shown as examples in the upper and lower panels in Fig. 3, respectively. The rotational structure of the $v' = 1$ band is typical of transitions between two Σ states, characterized by the rotational quantum numbers N'' and N' , respectively, and consists of overlapping P ($\Delta_{N'N''} = -1$) and R ($\Delta_{N'N''} = +1$) branches. These two branches are expected to overlap when the rotational constant of the final state is much smaller than that of the initial state, as in the present case (see Ref. 22 for a complete simulation of the band). The spectrum of the $v' = 14$ band consists, instead, of four distinct rotational branches, which indicates the departure of the B^+ state from Hund's coupling case (b). The rotational structure of the band can be well described by the four rotational branches that characterize transitions from a state described by Hund's coupling case (b) to a state described by Hund's coupling case (c). The branches are labeled $\Delta_{J'N''}$ and connect initial states with integer values of the total-angular-momentum without-spin quantum number N'' to final states with half-integer values of the total-angular-momentum quantum number J' .

The potential-energy functions $V_{\Sigma}(R)$ and $V_{\Pi}(R)$ in Eq. (4) can be represented by functions of the form

$$V_{\Lambda}(R) = A_{\Lambda} e^{-2\beta_{\Lambda}(R)(R-R_e^{\Lambda})} - C_{\Lambda} e^{-\beta_{\Lambda}(R)(R-R_e^{\Lambda})} + u_{\text{LR}}^{\Lambda}(R), \quad (5)$$

analogous to the double-exponential/long-range model potential described by Le Roy³⁶. A_{Λ} and C_{Λ} are obtained from the equilibrium distance R_e^{Λ} and the potential-well depth D_e^{Λ} using

$$A_{\Lambda} = D_e^{\Lambda} + u_{\text{LR}}^{\Lambda}(R_e^{\Lambda}) + \frac{1}{\beta_{\Lambda}(R_e^{\Lambda})} \left. \frac{du_{\text{LR}}^{\Lambda}}{dR} \right|_{R=R_e^{\Lambda}} \quad (6)$$

$$C_{\Lambda} = 2D_e^{\Lambda} + 2u_{\text{LR}}^{\Lambda}(R_e^{\Lambda}) + \frac{1}{\beta_{\Lambda}(R_e^{\Lambda})} \left. \frac{du_{\text{LR}}^{\Lambda}}{dR} \right|_{R=R_e^{\Lambda}}, \quad (7)$$

and the function $\beta_{\Lambda}(R)$ is given by

$$\beta_{\Lambda}(R) = B_{\Lambda} + \sum_{i=1}^{n_{\Lambda}} a_i^{\Lambda} \left(\frac{R^5 - R_{\text{ref}}^{\Lambda 5}}{R^5 + R_{\text{ref}}^{\Lambda 5}} \right)^i, \quad (8)$$

R_e^{Λ} , D_e^{Λ} , B_{Λ} and a_i^{Λ} being adjustable parameters of the model. In the present study, we fixed $R_{\text{ref}}^{\Sigma} = 6.3 a_0$ for

Table IV. Parameters describing the potential-energy functions of the A^+ and B^+ states of $MgAr^+$ according to Eqs. (4), (5), (8), (10) and (12). The parameters in the upper part of the table were obtained in a weighted least-squares fit to the experimental term values and rotational constants. The parameters in the lower part of the table were left fixed during the least-squares fit. All values are in atomic units. The weighted root-mean-square deviation of the fit was 1.3.

$V_\Sigma(R)$			$V_\Pi(R)$			$a(R)$	
Parameter	Value		Parameter	Value		Parameter	Value
R_e^Σ	8.352	a_0	R_e^Π	4.5263	a_0	H	$1.01 \times 10^{-5} E_h$
D_e^Σ	0.001 156 3	E_h	D_e^Π	0.025 672 7	E_h	S	6.38 a_0^{-1}
B_Σ	0.5164	a_0^{-1}	B_Π	0.985 02	a_0^{-1}	I	0.728 a_0
ρ_Σ	0.7	a_0^{-1}	ρ_Π	0.3742	a_0^{-1}		
a_1^Σ	0.05		a_1^Π	0.0716			
a_2^Σ	0.22		a_2^Π	0.0138			
			a_3^Π	0.0824			
R_{ref}^Σ	6.3	a_0	R_{ref}^Π	4.3	a_0		
C_6^Σ	47.44	$a_0^6 E_h$	C_6^Π	225.59	$a_0^6 E_h$		
α_{Ar}	11.077	a_0^3	α_{Ar}	11.077	a_0^3		

the Σ state and $R_{\text{ref}}^\Pi = 4.3 a_0$ for the Π state, corresponding to values at which the least-squares fits rapidly converged. Starting from $n_\Lambda = 1$, the number n_Λ of terms of the sum in Eq. (8) was systematically increased until agreement between the measured and calculated vibrational term values and rotational constants was reached. We found that setting $n_\Sigma = 2$ and $n_\Pi = 3$ was sufficient to reproduce the experimental results within experimental accuracy.

The long-range (LR) behavior of the potential is described by the function $u_{\text{LR}}^\Lambda(R)$ (see Eq. (5)), which accounts for the dominant electrostatic interactions between $Mg^+(3p)$ and Ar,

$$u_{\text{LR}}^\Lambda(R) = -\frac{\alpha_{Ar}}{2R^4} \phi_\Lambda^{(4)}(R) - \frac{C_6^\Lambda}{R^6} \phi_\Lambda^{(6)}(R). \quad (9)$$

The damping functions $\phi_\Lambda^{(m)}(R)$ progressively switch off electrostatic interactions at short internuclear distances, where covalent and repulsive forces dominate. We use the damping functions

$$\phi_\Lambda^{(m)} = \left[1 - \exp \left(-3.95 \frac{\rho_\Lambda R}{m} - 0.39 \frac{(\rho_\Lambda R)^2}{\sqrt{m}} \right) \right]^m, \quad (10)$$

similar to the one reported by Douketis *et al.*⁵⁰ (see also Le Roy *et al.*⁵¹). The system-dependent range-scaling parameters ρ_Λ ($\Lambda = 0, 1$) represent two additional adjustable parameters of the model. In Eq. (9), α_{Ar} is the static electric polarizability volume of the Ar atom ($\alpha_{Ar} = 11.077 a_0^{352}$), and $-\alpha_{Ar}/2r^4$ accounts for the charge-induced-dipole interaction in atomic units (E_h). The term $-C_6^\Lambda/r^6$ combines three electrostatic interactions: (i) the charge-induced-quadrupole interaction, (ii) the permanent-quadrupole-induced-dipole interaction, and (iii) the dispersion interaction. These interactions must be accounted for to correctly describe the interaction potentials of the electronic states of the np complexes of metal-rare-gas dimers (see, *e.g.*, Refs. 31,53).

The only value of C_6 available in the literature is the estimate of Le Roy²⁹ for the Π ($\Lambda = 1$) state, which does not include interaction (ii), and no value is available for the Σ ($\Lambda = 0$) state. We have therefore re-evaluated the values of the C_6^Λ coefficients by calculating independently the contribution of each interaction according to

$$C_6^\Lambda = \frac{\alpha_{Ar}^{(2)}}{2} + 3\Theta_{zz}^{(\Lambda)} \alpha_{Ar} + C_6^{\text{disp}}(\Lambda). \quad (11)$$

In Eq. (11), $\alpha_{Ar}^{(2)} = 50.21 a_0^5$ is the quadrupole polarizability of Ar⁵⁴ and $C_6^{\text{disp}}(\Lambda)$ is the Λ -dependent dispersion coefficient, calculated to be $205.5 E_h a_0^6$ for $\Lambda = 0$ and $108.9 E_h a_0^6$ for $\Lambda = 1$ ⁵⁵. $\Theta_{zz}^{(\Lambda)}$ is the permanent quadrupole moment of $Mg^+(3p)$ for a given value of Λ , *i.e.*, for a fixed value of the projection of the orbital angular momentum of the valence electron of Mg^+ onto the internuclear axis. For $\Lambda = 1$, we used the permanent quadrupole moment $\Theta_{zz}^{(1)} = 2.756 ea_0^2$, the absolute value of which was calculated by Mitroy and Zhang⁵⁵. From the value of $\Theta_{zz}^{(1)}$, we deduce that $\Theta_{zz}^{(0)}$, the quadrupole polarizability of $Mg^+(3p)$ for $\Lambda = 0$, is $-5.512 ea_0^2$ (see, *e.g.*, Medved *et al.*⁵⁶). Using Eq. (11) we obtain the values for the coefficients C_6^Λ listed in Table IV.

The spin-orbit coupling constant in Eq. (4) is described by the Morse-potential-type function

$$a(R) = H \left[1 - e^{-S(R-I)} \right]^2 - H + a_{\text{SO}}^{\text{Mg}^+}, \quad (12)$$

where $a_{\text{SO}}^{\text{Mg}^+} = \frac{2}{3} \cdot 91.57 \text{ cm}^{-1}$ is the $3p_{1/2} - 3p_{3/2}$ spin-orbit coupling constant in Mg^+ ⁴⁹. The parameters H , S and I in Eq. (12) are adjustable.

In total there are 16 adjustable parameters in the model (R_e^Λ , D_e^Λ , B_Λ , ρ_Λ , a_1^Λ , $\dots$, $a_{n_\Lambda}^\Lambda$, H , I and S , with $\Lambda = 0, 1$) that describe the three potentials $V_i(R)$ ($i = 1 - 3$)

corresponding to the eigenvalues of Eq. (4). The energies associated with the rotationless vibrational levels of each potential are calculated by numerically solving the nuclear Schrödinger equation

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + V_i(R) \right] \psi_{i,v}(R) = E_{i,v} \psi_{i,v}(R) \quad (13)$$

with a Legendre-Gauss-Lobatto discrete-variable-representation (DVR) technique^{57–60}. The rotational constants $B_{i,v}$ of each vibronic energy level are calculated from the expectation value of the $1/R^2$ operator, as described in 43.

Optimal values of the 16 model parameters are determined in a weighted nonlinear least-squares fit of the calculated energies and rotational constants to the corresponding experimental values, which comprise 154 data points in total. Initial values for these parameters were obtained by fitting the model potential-energy functions to the *ab initio* potential-energy curves of the A^+ and B^+ reported in the companion article²². Successive iterations were carried out during which only the parameters of either the V_{Π} , V_{Σ} or $a(R)$ functions were varied. Once a satisfactory set of parameters was obtained, all the parameters were optimized simultaneously in a global fit. In a last step, the parameters of the V_{Σ} potential were slightly re-optimized to reproduce the maxima and minimum of the photodissociation yield recorded above the dissociation threshold of the B^+ state (see Ref. 22). The relative photodissociation cross section was calculated from the B^+ adiabatic potential using a Legendre-Gauss-Lobatto finite-element DVR method with exterior complex scaling^{58,61} and under the assumption that the electronic transition moment is independent of R over the relevant range of internuclear distances. We made sure that this re-optimization had no influence on the accuracy of the potential-energy function in the region relevant for the bound states. This final step ensured that the potential describing the B^+ state is accurate for both bound states and continuum states corresponding to kinetic energy releases up to $E_{\text{KER}}/(hc) \simeq 300 \text{ cm}^{-1}$.

The optimal parameter values are presented in Table IV. The calculated term values and rotational constants corresponding to these parameters are compared to the experimental data obtained for the A^+ and B^+ states in Tables I and V, respectively. The vast majority of the calculated results are in agreement with experimental values within the error bars. The value of the weighted root-mean-square deviation⁶² is 1.3, which indicates that the model adequately describes the experimental data.

V. DISCUSSION

The potential-energy functions corresponding to the optimal values of the parameters are depicted in Fig. 4, where the positions of the measured vibrational energy levels are also indicated. The levels of the $A_{1/2}^+$ state

Figure 4. Potential energy curves of the first three electronic states of $^{24}\text{MgAr}^+$. The curve for the X^+ state was taken from Ref. 43. The curves of the $A_{\Omega'=1/2,3/2}^+$ and B^+ states were determined in the present work. The vibrational levels of the X^+ ⁴³, $A_{\Omega'=3/2}^+$ and B^+ ²² states that were observed experimentally are shown as the horizontal lines. The inset shows the bound part of the B^+ potential energy curve on an expanded scale.

are not shown for clarity. The $A_{1/2}^+$ and $A_{3/2}^+$ states are much more strongly bound ($D_e = 5612.1 \text{ cm}^{-1}$ and 5626.6 cm^{-1} , respectively) than the B^+ state ($D_e = 277.0 \text{ cm}^{-1}$). The equilibrium distances R_e of the $A_{1/2}^+$ and $A_{3/2}^+$ states ($4.524 a_0$ and $4.528 a_0$, respectively) are also significantly shorter than that of the B^+ state ($8.289 a_0$). The present values of both D_e and R_e are in good agreement with the *ab initio* calculations reported in the companion article²², which predict potential depths of $D_e = 5615.2 \text{ cm}^{-1}$, 5629.3 cm^{-1} and 253.2 cm^{-1} for the $A_{1/2}^+$, $A_{3/2}^+$ and B^+ states, respectively, and equilibrium distances of $R_e = 4.528 a_0$, $4.530 a_0$ and $8.560 a_0$.

The reason for the large differences between the A^+ and B^+ states has already been discussed^{22,24,25}, and can be qualitatively understood when considering the alignment of the $\text{Mg}^+(3p)$ orbital with respect to the internuclear axis. In the case of the A^+ state, the axis of

Table V. Observed band origins $\tilde{\nu}_{v'v''}$ of the $B^+(v') \leftarrow X^+(v'' = 7)$ transitions, taken from Ref. 22, term values $T_{v'}^{('obs)}$ of the B^+ -state levels with respect to the $A_{1/2}^+(v' = 0)$ ground vibrational level, and deviations $\Delta T_{v'}^{('2)} = T_{v'}^{('obs)} - T_{v'}^{('calc)}$ of the term values calculated using the potential-energy function determined in this article. The measured rotational constants $B_{v'}^{('obs)}$ of the $B^+(v')$ states are compared to the results obtained from the potential-energy function ($\Delta B_{v'}' = B_{v'}^{('obs)} - B_{v'}^{('calc)}$). All values are in cm^{-1} . The values in parentheses represent one standard deviation in units of the last digit.

v'	$\tilde{\nu}_{v'v''}$	$T_{v'}^{('obs)}$	$\Delta T_{v'}^{('2)}$	$B_{v'}^{('obs)}$	$\Delta B_{v'}'$
0	36 148.43(20)	5307.79(26)	-0.30	0.0608(10)	0.0030
1	36 181.34(20)	5340.70(26)	0.10	0.0550(20)	-0.0019
2	36 211.78(20)	5371.14(26)	0.05	0.0543(10)	-0.0015
3	36 240.31(20)	5399.67(26)	0.33	0.0521(10)	-0.0018
4	36 265.99(20)	5425.35(26)	0.13	—	—
5	36 289.44(20)	5448.80(26)	0.16	—	—
6	36 310.23(20)	5469.59(26)	0.02	—	—
7	36 328.53(20)	5487.89(26)	-0.14	0.0420(10)	-0.0019
8	36 344.53(20)	5503.89(26)	-0.16	0.0388(10)	-0.0018
9	36 358.28(20)	5517.64(26)	-0.08	0.0359(10)	-0.0015
10	36 369.52(20)	5528.88(26)	-0.29	0.0358(10)	0.0019
11	36 379.13(20)	5538.49(26)	-0.10	0.0324(10)	0.0014
12	36 386.73(20)	5546.09(26)	-0.09	0.0293(10)	0.0018
13	36 392.74(20)	5552.10(26)	-0.10	0.0212(10)	-0.0028
14	36 397.68(20)	5557.04(26)	0.18	0.0203(10)	-0.0006
15	36 401.25(20)	5560.61(26)	0.20	0.0187(10)	0.0015
16	36 403.92(20)	5563.28(26)	0.23	0.0190(20)	0.0044
17	36 405.95(40)	5565.31(43)	0.35	—	—
18	36 407.28(40)	5566.64(43)	0.35	—	—
19	36 407.80(40)	5567.16(43)	-0.02	—	—
20	36 408.25(40)	5567.61(43)	-0.12	—	—
21	36 408.85(40)	5568.21(43)	0.15	—	—

the $\text{Mg}^+(3p_\pi)$ orbital is perpendicular to the internuclear axis and leaves the Ar atom exposed to an unscreened Mg^{2+} core. At large R , this translates into an *attractive* interaction between the permanent quadrupole moment of $\text{Mg}^+(3p)$ and the induced dipole moment of Ar. The other dominant electrostatic interactions (charge – induced-dipole and charge – induced-quadrupole) are independent of the orbital alignment. In the case of the B^+ state, the axis of the p_σ orbital is parallel to the internuclear axis and almost perfectly screens, for the Ar atom, half of the charge of the Mg^{2+} core. At large R , this translates into a *repulsive* induced-dipole – permanent-quadrupole interaction. Moreover, because of the different alignment of the p orbital, the spatial overlap of the electronic clouds of Mg^+ and Ar, resulting in repulsive forces, is important at larger internuclear distances for the B^+ state than for the A^+ state.

The evolution of the two spin-orbit components of the A^+ state from Hund's coupling case (a) to Hund's coupling case (c) is well illustrated by the evolution of the $\Omega' = 1/2 - \Omega' = 3/2$ spin-orbit splitting with v' , as shown in Fig. 5. At low v' values, the vibrational

wave function is located near the equilibrium distance $R_e(A_{\Omega'}^+)$ and, in this region, the $A^+ {}^2\Pi_{1/2}$ state is hardly mixed with the $B^+ {}^2\Sigma^+$ state because the corresponding potential-energy functions lie energetically far apart. In this case, the $A_{1/2}^+ - A_{3/2}^+$ splitting is simply $a(R)$ (see diagonal elements in Eq. (4)). The observed low- v' splittings differ from $a(R \rightarrow \infty) = 61.05 \text{ cm}^{-1}$ because the spin-orbit constant $a(R)$ increases as R decreases. At higher v' , the vibrational wave function extends to larger internuclear distances, and is influenced by the $A^+ {}^2\Pi_{1/2} - B^+ {}^2\Sigma^+$ mixing, or equivalently by the transition from Hund's case (a) to Hund's case (c). The asymptotic spin-orbit splitting increases and reaches, asymptotically, $\frac{3}{2}a(R \rightarrow \infty) = 91.57 \text{ cm}^{-1}$, the spin-orbit splitting of the Mg^+ ion. The numerical values of all spin-orbit splittings determined in this work are listed in the supplementary material⁴⁶.

Precise values of the dissociation energies D_0 of the A^+ and B^+ states can be determined from the model potentials. They are compared in Table VI to values available in the literature. Because the experimental data for the B^+ state extend up to the dissociation limit and those for

Figure 5. Spin-orbit splitting between the $A_{1/2}^+(v')$ and $A_{3/2}^+(v')$ levels determined from the experimental (open circles) and calculated (crosses) term values. The limit of $\frac{3}{2}a(R \rightarrow \infty) = 91.57 \text{ cm}^{-1}$ is shown by the dashed gray line. It corresponds to the atomic $\text{Mg}^+(3p_{1/2} - 3p_{3/2})$ spin-orbit splitting and is asymptotically reached for high vibrational levels.

Table VI. Dissociation energies D_0 (in cm^{-1}) of the X^+ , A^+ and B^+ electronic states of $^{24}\text{MgAr}^+$ and of the $a^3\Pi_{0-}$ state of $^{24}\text{MgAr}$ determined from experimental data. In Ref. 29, the value of $D_0(X^+)$ was derived from $D_0(A^+)$ using a thermochemical cycle. This $D_0(X^+)$ value has been updated using the most recent experimental value of the electronic origin of the $A^+ \leftarrow X^+$ transition (see Refs. 21,43). The values in parentheses represent one standard deviation in units of the last digit.

State	D_0 / cm^{-1}	Ref.
$A_{1/2}^+$	5476.7(10)	this work
	5445(165)	Ref. 29
$A_{3/2}^+$	5491.5(10)	this work
	5460(165)	Ref. 29
B^+	260.2(10)	this work
X^+	1246.0(12)	this work
	1254(60)	Ref. 43
	1214(165)	Ref. 29
	1180(80)	Ref. 63
$a^3\Pi_{0-}$	1237(40)	Ref. 64
	167.6(11)	this work
	160(40)	Ref. 64

the A^+ states cover more than 90% of the total potential wells, the uncertainties on the D_0 values derived from the model potentials are small and estimated to be of the order of 1 cm^{-1} , which represents an improvement of more than two orders of magnitude in the uncertainties of $D_0(A_{1/2,3/2}^+)$ over previously available values²⁹. The

present D_0 values for the two spin-orbit components of the A^+ state are in agreement within error bars with the values determined by Le Roy²⁹ in a near-dissociation-expansion analysis of the $v' = 0 - 14$ term values measured by Pilgrim *et al.*^{24,25}. They are significantly larger than the spin-orbit-averaged value of 2983.39 cm^{-1} calculated by Gaied *et al.* using a pseudopotential approach³⁴. The present D_0 values are in very good agreement with the *ab initio* values of 5479.4 cm^{-1} and 5493.7 cm^{-1} reported in the companion article for the $\Omega' = 1/2$ and $3/2$ components, respectively²². No previous values for the dissociation energy of the B^+ state $D_0(B^+)$ were available in the literature before its observation in Ref. 22. The $D_0(B^+)$ value of $260.2(10) \text{ cm}^{-1}$ reported here is in reasonable agreement with the *ab initio* value of 237.7 cm^{-1} reported in Ref. 22.

The dissociation energy $D_0(X^+)$ of the X^+ ground state of MgAr^+ can be calculated to be $1246.0(12) \text{ cm}^{-1}$ from the dissociation energy $D_0(B^+)$ of the B^+ state using the thermochemical cycle

$$D_0(X^+) = \tilde{\nu}_{07} + T_7'' + D_0(B^+) - T(\text{Mg}^+, 3p_{3/2}). \quad (14)$$

In Eq. (14) the wave number $\tilde{\nu}_{07}$ of the $B^+(v' = 0) \leftarrow X^+(v'' = 7)$ transition is taken from Ref. 22, the term value T_7'' of the $X^+(v'' = 7)$ level is taken from Ref. 43, and $T(\text{Mg}^+, 3p_{3/2}) = 35760.88 \text{ cm}^{-1}$ is the term value of the $3p_{3/2}$ state of Mg^{+49} . The present value of the dissociation energy of the X^+ state is compared in Table VI to other experimental values or values determined from experimental data. Our new value is in excellent agreement with most previous ones, but much more precise. It is also in agreement with the latest *ab initio* value of 1238 cm^{-1} obtained by Tuttle *et al.*³⁵, and the value of 1235 cm^{-1} calculated by Gaied *et al.*³⁴.

The dissociation energy of the $a^3\Pi_{0-}$ metastable state of the neutral MgAr molecule can be determined in a similar way using

$$D_0(a) = \tilde{\nu}_{07} + \tilde{\nu}'_{70} + D_0(B^+) - \tilde{\nu}(\text{Mg}^+(3s_{1/2} - 3p_{3/2})) - E_i(\text{Mg}(3s3p^3P_0))/(hc), \quad (15)$$

where $E_i(\text{Mg}(3s3p^3P_0))$ is the ionization energy of the $3s3p^3P_0$ state of atomic Mg and $\tilde{\nu}'_{70}$ is the wave number of the $X^+(v'' = 7) \leftarrow a(v''' = 0)$ ionizing transition⁶⁵ reported in Ref. 43. The present value of $167.6(11) \text{ cm}^{-1}$ for $D_0(a)$ is in close agreement with the value of $160(40) \text{ cm}^{-1}$ reported by Massick and Breckenridge and estimated from the results of Birge-Sponer extrapolations and *ab initio* calculations⁶⁴.

In the companion article²², we showed that highly vibrational levels of the B^+ state ($v' \geq 7$) decay predominantly by spin-orbit predissociation into the $\text{Mg}^+(^2P_{1/2}) + \text{Ar}(^1S_0)$ continuum associated with the $\Omega' = 1/2$ spin-orbit component of the A^+ state (see inset in Fig. 4)²². This effect can be studied theoretically with the model presented in Sec. IV by diagonalizing the

part H_{SO} of the Hamiltonian in Eq. (4) corresponding to the spin-orbit interaction between $\Omega' = 1/2$ states in a basis of diabatic Hund's-coupling-case-(a) vibronic functions $|v', {}^2\Lambda'_{1/2}\rangle$. In doing so, we neglect heterogeneous perturbations. The matrix elements are

$$\langle v, {}^2\Sigma_{1/2} | H_{\text{SO}} | v', {}^2\Sigma_{1/2} \rangle = 0, \quad (16)$$

$$\langle v, {}^2\Pi_{1/2} | H_{\text{SO}} | v', {}^2\Sigma_{1/2} \rangle = \int dR (\chi_{\Pi}^v(R))^* \frac{a(R)}{\sqrt{2}} \chi_{\Sigma}^v(R), \quad (17)$$

$$\langle v, {}^2\Pi_{1/2} | H_{\text{SO}} | v', {}^2\Pi_{1/2} \rangle = - \int dR (\chi_{\Pi}^v(R))^* \frac{a(R)}{2} \chi_{\Pi}^v(R). \quad (18)$$

The vibrational wave functions χ_{Σ}^v and χ_{Π}^v are obtained by solving the nuclear Schrödinger equation (13) for the potentials V_{Σ} and V_{Π} , respectively. The basis set must include both bound and continuum vibrational wave functions, which we calculate using a Legendre-Gauss-Lobatto finite-element DVR technique with exterior complex scaling^{58,61}. Diagonalization of the large complex-symmetric diabatic matrix yields complex eigenvalues with, for the metastable vibrational levels of the B^+ state ($v' = 7 - 21$), a real part equal to the energy of the level $E_{v'}$ and an imaginary part equal to $-\Gamma_{v'}/2$, where $\Gamma_{v'}$ is the predissociation width. The predissociation widths are found to lie in the range from 0.03 cm^{-1} to 0.0003 cm^{-1} , depending on v' , which corresponds to lifetimes between 18 ns and $1.8 \mu\text{s}$. These values agree with the experimental observations that (i) the broadening of individual lines in the measured spectra resulting from predissociation is equal to or smaller than the laser linewidth of 0.1 cm^{-1} and (ii) the predissociation rate is faster than the time scale of the experiment ($\sim 5 \mu\text{s}$)²². The values of the calculated widths $\Gamma_{v'}$ are listed in the supplementary material⁴⁶. The positions of the predissociative vibrational levels of the B^+ state ($v' \geq 7$) calculated using either the adiabatic potential or the method just described differ by less than 0.25 cm^{-1} , *i.e.*, by less than the experimental uncertainties of the measured term values. Lower-lying levels ($v' = 0 - 6$) differ by at most 0.4 cm^{-1} . Therefore, non-adiabatic corrections to the adiabatic vibrational energies are small, as expected from the fact that the weighted root-mean-square deviation of the fit ($\simeq 1.3$) of the potential-energy functions described in Sec. IV is close to unity.

VI. CONCLUSION

We reported a global study of the $3p$ Rydberg complex of the MgAr^+ molecular ion. Using the ICMRD technique, high-resolution spectroscopic data were obtained for the two spin-orbit components of the A^+ state, up to vibrational levels as high as $v' = 29$. Combined with the data reported on the B^+ state in the companion article²², they give a complete and detailed picture of the

$3p$ Rydberg complex. Potential-energy functions were extracted from the experimental energies and rotational constants in a direct-potential-fit approach that included the R -dependent spin-orbit interaction between the three states of the complex. These potential-energy functions reproduce the positions of all observed vibrational levels of the $A^+_{1/2}$, $A^+_{3/2}$ and B^+ states to within less than 0.5 cm^{-1} .

The dissociation limits of the B^+ state and of the two spin-orbit components of the A^+ state were determined from the fitted potential-energy functions and have uncertainties of only 1 cm^{-1} , *i.e.*, they are more precise than previous works by more than two orders of magnitude²⁹. Dissociation limits with significantly reduced uncertainties could also be determined for the $X^+ {}^2\Sigma^+$ state of MgAr^+ and the $a {}^3\Pi_0^-$ state of MgAr . Finally, the non-adiabatic effects caused by the spin-orbit coupling between the B^+ and A^+ states were investigated theoretically and provided results in excellent agreement with the experimental ones²².

The $4s$, $3d$ and $4p$ Rydberg complexes of MgAr^+ lie energetically about 30000 cm^{-1} above the $3p$ complex. Their investigation by ICMRD from the A^+ or B^+ states is under way. The $4s$ and $3d$ complexes lie in the same region of energy as charge-transfer states correlated to the $\text{Mg}({}^1S_0) + \text{Ar}^+({}^2P_{3/2,1/2})$ dissociation asymptotes. The investigation of these charge transfer states by ICMRD may be possible by detecting the pulsed field ionization of the Ar fragment in high Rydberg states, instead of the Mg fragment in high Rydberg states as in the present work.

Such an investigation would enable the characterization of the effects of charge-transfer interaction on the Rydberg states of molecular ions. Exciting the molecular ion even further, we expect that the ground electronic state of the doubly-charged MgAr^{2+} ion can be reached and investigated by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy, following the procedure we recently tested with Mg^{+42} . This procedure is general and can be applied to molecular cations other than MgAr^+ in future work. The investigation of doubly-charged molecular ions by high-resolution photoelectron spectroscopy would permit the exploration of the diversity and complexity of the mechanisms responsible for the stability or instability of such systems, as illustrated in the Fig. 1 of the companion article²² and discussed by Schröder and Schwarz⁶⁶.

SUPPLEMENTARY MATERIAL

See the supplementary material for tables listing the molecular constants of the A^+ and B^+ states, the v -dependent spin-orbit splittings and spin-orbit-averaged term values of the A^+_{Ω} states and the calculated nonadiabatic spin-orbit-predissociation widths of the vibrational levels of the B^+ state.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article and its supplementary material.

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