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# Infrared spectra of mass-selected $\text{Mg}^+-\text{H}_2$ and $\text{Mg}^+-\text{D}_2$ complexes

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# Infrared spectra of mass-selected Mg<sup>+</sup>-H<sub>2</sub> and Mg<sup>+</sup>-D<sub>2</sub> complexes

## Abstract

Rotationally resolved infrared spectra of Mg<sup>(+)</sup>-H<sub>2</sub> and Mg<sup>(+)</sup>-D<sub>2</sub> are recorded in the H-H (4025-4080 cm<sup>(-1)</sup>) and D-D (2895-2945 cm<sup>(-1)</sup>) stretch regions by monitoring Mg<sup>(+)</sup> photofragments. The ν(HH) and ν(DD) transitions of Mg<sup>(+)</sup>-H<sub>2</sub> and Mg<sup>(+)</sup>-D<sub>2</sub> are red-shifted by 106.2 ± 1.5 and 76.0 ± 0.1 cm<sup>(-1)</sup> respectively from the fundamental vibrational transitions of the free H<sub>2</sub> and D<sub>2</sub> molecules. The spectra are consistent with a T-shaped equilibrium structure in which the Mg<sup>(+)</sup> ion interacts with a slightly perturbed H<sub>2</sub> or D<sub>2</sub> molecule. From the spectroscopic constants, a vibrationally averaged intermolecular separation of 2.716 Å (2.687 Å) is deduced for the ground state of Mg<sup>(+)</sup>-H<sub>2</sub> (Mg<sup>(+)</sup>-D<sub>2</sub>), decreasing by 0.037 Å (0.026 Å) when the H<sub>2</sub> (D<sub>2</sub>) subunit is vibrationally excited.

## Keywords

d<sub>2</sub>, spectra, complexes, mass, h<sub>2</sub>, infrared, selected, mg, GeoQUEST

## Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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# Infrared Spectra of Mass-Selected $\text{Mg}^+-\text{H}_2$ and $\text{Mg}^+-\text{D}_2$ Complexes

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Rotationally resolved infrared spectra of  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  are recorded in the H–H (4025–4080  $\text{cm}^{-1}$ ) and D–D (2895–2945  $\text{cm}^{-1}$ ) stretch regions by monitoring  $\text{Mg}^+$  photofragments. The  $\nu_{\text{HH}}$  and  $\nu_{\text{DD}}$  transitions of  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  are red-shifted by  $106.2 \pm 1.5$  and  $76.0 \pm 0.1$   $\text{cm}^{-1}$  respectively from the fundamental vibrational transitions of the free  $\text{H}_2$  and  $\text{D}_2$  molecules. The spectra are consistent with a T-shaped equilibrium structure in which the  $\text{Mg}^+$  ion interacts with a slightly perturbed  $\text{H}_2$  or  $\text{D}_2$  molecule. From the spectroscopic constants, a vibrationally averaged intermolecular separation of 2.716 Å (2.687 Å) is deduced for the ground state of  $\text{Mg}^+-\text{H}_2$  ( $\text{Mg}^+-\text{D}_2$ ), decreasing by 0.037 Å (0.026 Å) when the  $\text{H}_2$  ( $\text{D}_2$ ) subunit is vibrationally excited.

## 1. Introduction

Interactions between metal cations and neutral molecules play key roles in a variety of contexts including gas storage in solid materials, ion solvation, laser plasmas, and atmospheric and astrophysical processes. One route for characterizing the interactions between metal cations ( $\text{M}^+$ ) and neutral molecules (L) is to form and spectroscopically probe  $\text{M}^+-\text{L}_n$  complexes in the gas phase. Complexes containing the magnesium cation have played an important role in this program. The studies, which have embraced  $\text{Mg}^+$  attached to Ar,  $\text{H}_2$ , O,  $\text{D}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_2\text{O}$ , and pyridine, have usually entailed exciting the  $^2P \leftarrow ^2S$  electronic transitions centered on the  $\text{Mg}^+$  ion.<sup>1–5</sup> Recently, complexes such as  $\text{Mg}^+(\text{H}_2\text{O})_n$  have also been probed through their infrared absorptions in the O–H stretch region.<sup>6</sup>

In this paper, spectroscopic studies of charged complexes containing the magnesium cation are extended to include  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$ , which are probed by using infrared (IR) photodissociation spectroscopy in the H–H and D–D stretch regions, respectively. The resulting spectra feature full rotational resolution giving access to vibrationally averaged intermolecular bond lengths, the H–H and D–D stretch vibrational frequencies, and estimates for the intermolecular stretch vibrational frequencies. The ensuing data should serve to test potential energy surfaces for the  $\text{Mg}^+\cdots\text{H}_2$  interaction and complement recent spectroscopic and theoretical investigations of other metal cation–dihydrogen complexes including  $\text{Li}^+-\text{H}_2$ ,  $\text{Al}^+-\text{H}_2$ ,  $\text{B}^+-\text{H}_2$ , and  $\text{Na}^+-\text{H}_2$ .<sup>7–11</sup>

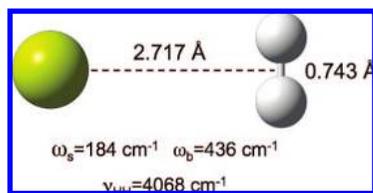
A more comprehensive understanding of the interaction between  $\text{Mg}^+$  and  $\text{H}_2$  is desirable for several reasons. Perhaps most important are insights into hydrogen storage materials containing magnesium, including metal hydrides,<sup>12,13</sup> metal–organic frameworks,<sup>14,15</sup> and metal cation-doped zeolites.<sup>16,17</sup> Areán and co-workers have examined  $\text{H}_2$  absorption in a magnesium-containing zeolite using variable-temperature FTIR spectroscopy.<sup>16</sup> By monitoring the intensity of the H–H stretch vibrational band associated with  $\text{H}_2$  attached to the  $\text{Mg}^{2+}$  sites (4056  $\text{cm}^{-1}$ ), the standard enthalpy of  $\text{H}_2$  adsorption was found to be  $-18.2$  kJ/mol, considerably higher in magnitude than that for  $\text{Li}^+$  and  $\text{Na}^+$  sites in zeolites. The binding energy is, however, far lower than that for the interaction between  $\text{Mg}^{2+}$

and  $\text{H}_2$  in the gas phase for which calculations give values closer to  $-92$  kJ/mol.<sup>18,19</sup> Although the formal charge of Mg ions in the zeolites is  $2+$ , charge transfer from the surrounding framework inevitably reduces the effective charge and magnitude of the adsorption enthalpy.

In the only previous spectroscopic investigation, the electronic transitions of  $\text{Mg}^+-\text{D}_2$  were probed over the 280–315 nm range by monitoring  $\text{MgD}^+$  photofragments.<sup>2,20</sup> The spectrum displayed a long vibrational progression associated with the  $^2B_1 \leftarrow ^2A_1$  transition superimposed on a broad continuum background associated with the  $^2B_2 \leftarrow ^2A_1$  transition. The vibrational progression, which exhibited an interval that decreased from 489 to 314  $\text{cm}^{-1}$ , was assigned to the intermolecular stretch in the  $^2B_1$  state. Overall, the spectral features were quite broad making it difficult to derive detailed structural information. In recent related work, reactions between laser-cooled  $\text{Mg}^+$  ions in the excited 3p state and  $\text{H}_2$ ,  $\text{D}_2$ , and HD molecules have been investigated.<sup>21</sup> Intriguingly, reactions between  $\text{Mg}^+$  and HD preferentially produce  $\text{MgD}^+$  rather than  $\text{MgH}^+$ . The  $\text{Mg}^+-\text{H}_2$  complex has also been considered as a possible constituent of the interstellar medium with Petrie and Dunbar concluding that radiative association of  $\text{Mg}^+$  and  $\text{H}_2$  proceeds too slowly for the formation of appreciable  $\text{Mg}^+-\text{H}_2$  abundances.<sup>22</sup>

There have been several ab initio studies of  $\text{Mg}^+-\text{H}_2$  giving disparate structural parameters. Originally, HF/6-31G\* level calculations by Curtiss and Pople predicted that  $\text{Mg}^+-\text{H}_2$  is a T-shaped,  $C_{2v}$  complex with a relatively long  $\text{Mg}^+\cdots\text{H}_2$  intermolecular bond (3.73 Å), and a binding energy of 200  $\text{cm}^{-1}$ .<sup>23</sup> Later, more reliable CASSCF calculations by Bauschlicher confirmed the T-shaped structure but suggested a much shorter intermolecular bond of 2.72 Å, a dissociation energy of 525  $\text{cm}^{-1}$ , and an H–H bond that is 0.006 Å longer than that of the free  $\text{H}_2$  molecule.<sup>24</sup> Subsequently, Petrie and Dunbar reported rotational constants determined at the MP2(full)/6-31G\* level that are compatible with an intermolecular bond length of 3.48 Å. Spectroscopic investigations described in this paper provide empirical values for the intermolecular separation and intermolecular stretch vibrational frequency allowing a critical assessment of the earlier calculations.

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**Figure 1.** Geometrical parameters and vibrational frequencies for  $\text{Mg}^+\text{-H}_2$  calculated at the MP2/aug-cc-pVTZ level. Note that the H–H stretch frequency has been scaled by 0.921 (see Section 2).

## 2. Experimental and Theoretical Approaches

Infrared spectra of  $^{24}\text{Mg}^+\text{-H}_2$  and  $^{24}\text{Mg}^+\text{-D}_2$  were obtained by monitoring  $^{24}\text{Mg}^+$  photodissociation products while scanning the IR wavelength over the H–H or D–D stretch region. The complexes were generated in a supersonic expansion of  $\text{H}_2$  or  $\text{D}_2$  (8 bar) passed over a laser-ablated magnesium rod. The translating/rotating rod was irradiated with the fundamental (1064 nm, 7 mJ/pulse), doubled (532 nm, 3 mJ/pulse), and quadrupled (266 nm, 1 mJ/pulse) output of a pulsed Nd:YAG laser running at 20 Hz. The  $\text{Mg}^+\text{-H}_2$  and  $\text{Mg}^+\text{-D}_2$  complexes were mass-selected by a quadrupole mass filter and deflected through  $90^\circ$  by a quadrupole bender into an octopole ion guide where they were overlapped by the counterpropagating output of a pulsed, tunable IR optical parametric oscillator (Continuum Mirage 3000, bandwidth of  $0.017\text{ cm}^{-1}$ ). The  $\text{Mg}^+$  photofragments were mass-selected by a second quadrupole mass filter and detected by using a microchannel plate coupled to a scintillator and a photomultiplier tube. The observed transition intensities were not normalized for laser power or parent ion flux (which exhibits shot-to-shot and longer term fluctuations). Spectral calibration was achieved by using previously described methods.<sup>7</sup> The absolute uncertainty of the line wavenumbers is decided by the uncertainty of the ion energy in the octopole ion guide and is estimated as  $\pm 0.10\text{ cm}^{-1}$ .

One difficulty associated with recording the  $^{24}\text{Mg}^+\text{-H}_2$  spectrum stems from the presence of isobaric  $^{26}\text{Mg}^+$  ions (11% natural abundance) which are present in far higher abundance than the target complex. Slight transmission of  $^{26}\text{Mg}^+$  ions through the second quadrupole mass filter leads to an appreciable background signal that degrades the  $^{24}\text{Mg}^+\text{-H}_2$  spectrum. This problem does not occur for  $^{24}\text{Mg}^+\text{-D}_2$  and consequently the signal-to-noise ratio of the  $^{24}\text{Mg}^+\text{-D}_2$  spectrum is somewhat better than that of the  $^{24}\text{Mg}^+\text{-H}_2$  spectrum.

Ab initio calculations for  $\text{Mg}^+\text{-H}_2$  were carried out by using the MP2 method with the Dunning aug-cc-pVTZ basis set and employed the Gaussian 03 suite of programs.<sup>25</sup> The dissociation energy for  $\text{Mg}^+\text{-H}_2$  was calculated taking into account harmonic zero-point energies but ignoring basis set superposition error. The calculated H–H stretch vibrational frequency was scaled by the factor required to reconcile the calculated and experimental frequencies for the free  $\text{H}_2$  molecule (0.921).

## 3. Results

**3.1.  $\text{Mg}^+\text{-H}_2$ .** The calculated equilibrium structure and harmonic vibrational frequencies of  $\text{Mg}^+\text{-H}_2$  are shown in Figure 1. In accordance with previous theoretical studies,  $\text{Mg}^+\text{-H}_2$  is predicted to have a T-shaped,  $C_{2v}$  equilibrium structure with the  $\text{Mg}^+$  ion attached to a weakly perturbed  $\text{H}_2$  molecule.

The energy levels of the  $\text{Mg}^+\text{-H}_2$  complex in the  $^2A_1$  ground electronic state can be labeled by using quantum numbers appropriate for a doublet, near-prolate, asymmetric rotor ( $J$ ,  $N$ ,  $K_a$ , and  $K_c$ ). For Hund's Case (b) coupling, the total angular

momentum excluding nuclear spin ( $\hat{J}$ ) is related to the rotational angular momentum ( $\hat{N}$ ) and the total electronic spin ( $\hat{S}$ ) by  $\hat{J} = \hat{N} + \hat{S}$ . The quantum numbers  $K_a$  and  $K_c$  describe the projections of the rotational angular momentum along the  $a$  and  $c$  axes in the prolate and oblate top limits, respectively. For the  $\text{Mg}^+\text{-H}_2$  complex, the  $a$ -axis corresponds to the intermolecular axis.

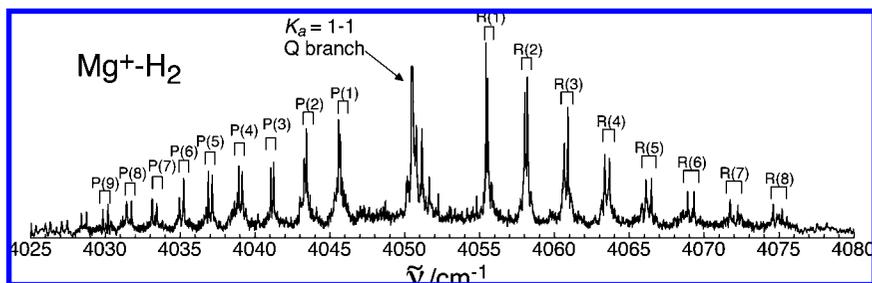
Each rotational  $N$  value is associated with  $J = N - 1/2$  and  $J = N + 1/2$  sublevels that are separated due to coupling between the electronic spin and molecular rotation. The MP2/aug-cc-pVTZ ab initio calculations for  $\text{Mg}^+\text{-H}_2$  suggest that the electronic spin-rotation splitting is small (predicted constants are  $\epsilon_{aa} = -1.34 \times 10^{-3}\text{ cm}^{-1}$ ,  $\epsilon_{bb} = 1.2 \times 10^{-4}\text{ cm}^{-1}$ , and  $\epsilon_{cc} = 1.0 \times 10^{-4}\text{ cm}^{-1}$ ) and indeed we are unable to resolve spin-rotation splitting in the  $\text{Mg}^+\text{-H}_2$  and  $\text{Mg}^+\text{-D}_2$  infrared spectra. Therefore, spin-rotation coupling is disregarded in the subsequent analysis and the energy levels are labeled only with the quantum numbers  $N$ ,  $K_a$ , and  $K_c$ .

Because the transition moment associated with excitation of the H–H stretch lies along the  $a$ -axis, the infrared transitions of  $\text{Mg}^+\text{-H}_2$  are characteristic of a parallel  $A$ -type transition and follow  $\Delta K_a = 0$  and  $\Delta K_c = \pm 1$  selection rules. For transitions originating from  $K_a = 0$  and  $K_a \geq 1$  states, the total angular momentum selection rules are  $\Delta J = \pm 1$  and  $\Delta J = 0, \pm 1$ , respectively. Selection rules for  $N$  are identical with those for  $J$ .

The infrared spectrum of  $\text{Mg}^+\text{-H}_2$  over the  $4025\text{--}4080\text{ cm}^{-1}$  range is shown in Figure 2. The spectrum exhibits well-resolved rovibrational features belonging to the  $K_a = 1\text{--}1$  sub-band, associated with complexes containing the ortho form of  $\text{H}_2$  (odd  $j$  levels). There is no trace of the  $K_a = 0\text{--}0$  sub-band associated with complexes containing para  $\text{H}_2$  (even  $j$  levels). A similar preponderance of complexes containing ortho  $\text{H}_2$  has been observed for other neutral and charged complexes<sup>9,26,27</sup> and, in part, reflects the 1:3 para/ortho population ratio in normal hydrogen gas. Furthermore, a free  $\text{H}_2$  molecule in the  $j = 1$  state has  $\sim 120\text{ cm}^{-1}$  more rotational energy than a  $j = 0$   $\text{H}_2$  molecule; this rotational energy is partially quenched in the complex leading to a stabilization of  $\text{Mg}^+\text{-H}_2$  (ortho) relative to  $\text{Mg}^+\text{-H}_2$  (para). Therefore,  $\text{Mg}^+\text{-H}_2$  (para) complexes are likely to be converted to the more stable  $\text{Mg}^+\text{-H}_2$  (ortho) complexes in the ion source through rapid, exothermic, ligand switching reactions.

Altogether, 38 transitions were assigned to the  $K_a = 1\text{--}1$  sub-band (22 P-branch and 16 R-branch lines), with asymmetry doublets resolved in the P and R branches. The Q-branch lines were overlapped and were excluded from the fit. Transition wavenumbers and assignments are provided as Supporting Information. The  $K_a = 1\text{--}1$  transitions of  $\text{Mg}^+\text{-H}_2$  were fitted by using an  $A$ -reduced Watson Hamiltonian with adjustable parameters including the ground and excited state  $B$ ,  $C$ , and  $\Delta_J$  rotational constants. It is not possible to determine the ground and excited state  $A$  rotational constants through analysis of the parallel transition. Therefore for the fit,  $A''$  and  $A'$  were constrained to  $59.34\text{ cm}^{-1}$ , the rotational constant of free  $\text{H}_2$  in the  $n_{\text{HH}} = 0$  state.<sup>28</sup> Note that the fits are insensitive to the absolute values of  $A''$  and  $A'$ ; virtually identical  $B$ ,  $C$ , and  $\Delta_J$  values are obtained for  $A''$  and  $A'$  ranging from  $50$  to  $70\text{ cm}^{-1}$ . Resulting spectroscopic constants for  $\text{Mg}^+\text{-H}_2$  are listed in Table 1.

Because no  $K_a = 0\text{--}0$  transitions were observed for  $\text{Mg}^+\text{-H}_2$ , the  $\nu_{\text{HH}}$  band center cannot be determined directly. However, it is estimated to lie between  $\Delta b$  and  $2\Delta b$  above the  $K_a = 1\text{--}1$  sub-band center ( $4050.5\text{ cm}^{-1}$ ). Here,  $\Delta b \approx 3\text{ cm}^{-1}$  is the difference in the  $\text{H}_2$  rotational constant in the  $n_{\text{HH}} = 0$  and 1

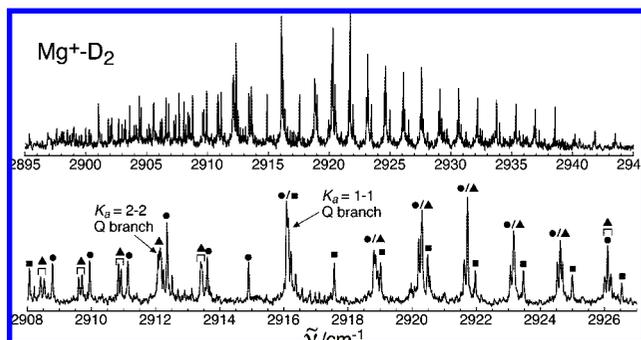


**Figure 2.** Infrared spectrum of  $^{24}\text{Mg}^+-\text{H}_2$  in the H-H stretch region obtained by monitoring  $\text{Mg}^+$  photofragments. The  $K_a = 1-1$  P, Q, and R branch transitions are labeled.

**TABLE 1: Spectroscopic Constants (in  $\text{cm}^{-1}$  unless otherwise indicated) for  $^{24}\text{Mg}^+-\text{H}_2$  and  $^{24}\text{Mg}^+-\text{D}_2$  Obtained by Fitting the  $\nu_{\text{HH}}$  and  $\nu_{\text{DD}}$  Transitions to a Watson A-Reduced Hamiltonian<sup>a</sup>**

	$\text{Mg}^+-\text{H}_2$		$\text{Mg}^+-\text{D}_2$		
	$K_a=1-1$	$K_a=0-0$	$K_a=1-1$	$K_a=2-2$	$K_a=0-0, 1-1$
$B''$	1.2411(14)		0.6807(11)		0.6804(11)
$C''$	1.1916(14)		0.6587(11)		0.6584(11)
$\bar{B}''$	1.2164(14)	0.6708(12)	0.6697(11)	0.6679(14)	0.6694(11)
$\Delta''_J \times 10^4$	1.925(42)	0.57(4)	0.527(32)	0.540(40)	0.514(20)
$\Delta''_{JK} \times 10^4$					-1.39(49)
$B'$	1.2762(14)		0.6941(11)		0.6937(11)
$C'$	1.2233(14)		0.6708(11)		0.6705(11)
$\bar{B}'$	1.2498(14)	0.6836(12)	0.6824(11)	0.6799(14)	0.6821(11)
$\Delta'_J \times 10^4$	1.751(51)	0.53(4)	0.503(32)	0.492(36)	0.471(23)
$\Delta'_{JK} \times 10^4$					-3.14(39)
$\Delta A$					1.464(12)
$\nu_{\text{sub}}$	4050.46(1)	2917.56(2)	2916.09(1)	2912.05(2)	2917.55(1)
rms $\times 10^3$	4.8	3.5	7.6	2.6	10.5
$\Delta\nu_{\text{HH}}$	-106.2(1.5)				-76.0(0)
$\omega''_s$	193				153
$\omega'_s$	211				164
$R''_0/\text{\AA}$	2.716				2.687
$R'_0/\text{\AA}$	2.679				2.661

<sup>a</sup> For each value, the error in the last significant figure(s) is given in parentheses.



**Figure 3.** Top: Infrared spectrum of  $^{24}\text{Mg}^+-\text{D}_2$  in the D-D stretch region obtained by monitoring  $\text{Mg}^+$  photofragments. Bottom: Expanded central region of the  $\text{Mg}^+-\text{D}_2$  spectrum. The  $K_a = 0-0$  (circles),  $1-1$  (triangles), and  $2-2$  (squares) transitions are labeled.

states, and the lower and upper limits are based on the  $\text{Mg}^+-\text{H}_2$  complex being a rigid prolate rotor or containing a freely rotating hydrogen subunit, respectively. For the moment, the band center is deemed as the average of the lower and upper limits (i.e.,  $4055.0 \text{ cm}^{-1}$ ). This corresponds to a red-shift of  $106.2 \text{ cm}^{-1}$  with respect to the  $Q_1(0)$  transition of the free  $\text{H}_2$  molecule ( $4161.2 \text{ cm}^{-1}$ ).<sup>29</sup>

**3.2.  $\text{Mg}^+-\text{D}_2$ .** The infrared spectrum of  $\text{Mg}^+-\text{D}_2$  over the  $2895-2945 \text{ cm}^{-1}$  range is shown in Figure 3. Many more transitions are observed for  $\text{Mg}^+-\text{D}_2$  than for  $\text{Mg}^+-\text{H}_2$ , with  $K_a = 0-0$ ,  $1-1$ , and  $2-2$  transitions all appearing in the spectrum. The presence of the  $K_a = 0$  and  $2$  complexes in detectable abundances for  $\text{Mg}^+-\text{D}_2$  but not for  $\text{Mg}^+-\text{H}_2$  is a

consequence of a better signal-to-noise ratio of the  $\text{Mg}^+-\text{D}_2$  spectrum (see Section 2), the fact that the population ratio of even to odd  $j$  levels in  $\text{D}_2$  is 2:1 rather than 1:3 in  $\text{H}_2$ , and because the ligand switching reaction which favors the  $K_a = 1$  complexes is less exothermic for  $\text{D}_2$  than for  $\text{H}_2$ . Altogether, 79 transitions were assigned to the  $K_a = 0-0$  (14 P-branch and 14 R-branch lines),  $K_a = 1-1$  (18 P-branch and 20 R-branch lines), and  $K_a = 2-2$  (6 P-branch and 7 R-branch lines) sub-bands. Asymmetry doublets were resolved in the P and R branches of the  $K_a = 1-1$  sub-band, but not the  $K_a = 2-2$  sub-band.

As described above for  $\text{Mg}^+-\text{H}_2$ , the transitions of  $\text{Mg}^+-\text{D}_2$  were fitted by using an A-reduced Watson Hamiltonian. For fitting the sub-bands individually,  $A''$  and  $A'$  were constrained to  $29.907 \text{ cm}^{-1}$ , the ground state rotational constant of the free  $\text{D}_2$  molecule.<sup>28</sup> When two or more sub-bands were fitted together,  $A''$  was constrained to  $29.907 \text{ cm}^{-1}$  while  $A'$  was allowed to vary. The fit of a parallel transition can only yield  $\Delta A = A' - A''$  and is relatively insensitive to the absolute values of  $A''$  and  $A'$ . A reasonable fit was obtained for the  $K_a = 0-0$  and  $1-1$  sub-bands together (rms =  $1.0 \times 10^{-2} \text{ cm}^{-1}$ ); however the fit deteriorated when the  $K_a = 2-2$  transitions were also included (rms =  $4.2 \times 10^{-2} \text{ cm}^{-1}$ ), despite the latter sub-band giving a good fit by itself. The difficulty in fitting simultaneously the  $K_a = 0-0$ ,  $1-1$ ,  $2-2$  transitions by using a limited number of adjustable parameters is presumably a consequence of the large-amplitude bending motion of the floppy complex. Resulting spectroscopic constants for  $\text{Mg}^+-\text{D}_2$  are listed in Table 1.

**TABLE 2: Calculated and measured properties of  ${}^2\text{Mg}^+-\text{H}_2$** 

	exptl <sup>1</sup>	MP2/ aug-cc-pVTZ <sup>a</sup>	CASSCF <sup>b</sup>	MP2(full)/ 6-31G* <sup>c</sup>
$\omega_s/\text{cm}^{-1}$	193	184	180	69
$\omega_b/\text{cm}^{-1}$		436	410	124
$\Delta\nu_{\text{HH}}/\text{cm}^{-1}$	-106.2	-93	-85	
$R_e/\text{\AA}$		2.72	2.72	3.48
$R_0/\text{\AA}$	2.716			
$D_0/\text{\AA}$		416	525	485

<sup>a</sup> Current work. <sup>b</sup> Reference 30.  $\Delta\nu_{\text{HH}}$  is based on a scaled  $\nu_{\text{HH}}$  frequency (scaling factor = 0.945). <sup>c</sup> Reference 22.

Transition wavenumbers and assignments are provided as Supporting Information.

The  $\nu_{\text{DD}}$  transition for  $\text{Mg}^+-\text{D}_2$  occurs at  $2917.6\text{ cm}^{-1}$  corresponding to a shift of  $\Delta\nu_{\text{DD}} = -76.0\text{ cm}^{-1}$  from the  $Q_1(0)$  transition of the free  $\text{D}_2$  molecule ( $2993.6\text{ cm}^{-1}$ ). The ratio of the  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  shifts  $\Delta\nu_{\text{HH}}/\Delta\nu_{\text{DD}} = 1.40$  is close to the ratio expected if the H-H and D-D stretch modes are decoupled from the remaining vibrational modes ( $\Delta\nu_{\text{HH}}/\Delta\nu_{\text{DD}} = (m_{\text{D}}/m_{\text{H}})^{1/2} = 1.41$ ).

## 4. Discussion

### 4.1. Structural, Energetic, and Vibrational Properties.

Overall, the spectroscopic data confirm that  $\text{Mg}^+-\text{H}_2$  is a T-shaped complex consisting of a  $\text{Mg}^+$  ion attached to a slightly perturbed  $\text{H}_2$  molecule by charge-quadrupole electrostatic and charge-induced-dipole induction interactions. Evidence for the weak nature of the intermolecular bond is that the  $\text{H}_2$  vibrational frequency is reduced by only 2.6% and that the vibrationally averaged intermolecular bond length deduced from the  $B$  and  $C$  rotational constants ( $2.716\text{ \AA}$ ) is typical for complexes of this type.<sup>18</sup> Generally, the properties of  $\text{Mg}^+-\text{D}_2$  are similar to those of  $\text{Mg}^+-\text{H}_2$  although it possesses a slightly shorter vibrationally averaged intermolecular bond (by  $0.029\text{ \AA}$ ), presumably due to reduced zero-point vibrational motion in the intermolecular stretch coordinate. The intermolecular bonds of  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  shorten upon vibrational excitation of the diatomic subunit (by  $0.037$  and  $0.026\text{ \AA}$ , respectively); this can be seen as a consequence of enhancements to the electrostatic and induction interactions following increases in the quadrupole moments and polarizabilities of  $\text{H}_2$  and  $\text{D}_2$  in their excited vibrational states.

Unfortunately, the  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  infrared spectra provide no information on the H-H and D-D bond distances. For a completely rigid T-shaped complex it is possible to deduce the  $A$  rotational constant and therefore the H-H separation from  $B$  and  $C$  as the inertial defect  $\Delta = 1/C - 1/B - 1/A$  is zero. However, the large-amplitude zero-point bending motion in  $\text{Mg}^+-\text{H}_2$  leads to an exaggeration of the asymmetry spitting and a nonzero inertial defect rendering it impossible to deduce  $A$ .<sup>26,31</sup> However, on the basis of the MP2/aug-cc-pVTZ calculations, the H-H bond is predicted to lengthen by  $0.006\text{ \AA}$  compared to the free  $\text{H}_2$  molecule ( $0.737\text{ \AA}$ ).

Measured and calculated structural and vibrational properties of  $\text{Mg}^+-\text{H}_2$  are summarized in Table 2. Generally, the measured properties are consistent with the MP2/aug-cc-pVTZ results and the earlier CASSCF calculations of Bauschlicher, with good agreement for the vibrational red-shift  $\Delta\nu_{\text{HH}}$ , the harmonic intermolecular stretch frequency ( $\omega_s$ ), and the intermolecular separation. The  $\text{Mg}^+-\text{H}_2$  vibrationally averaged intermolecular separation  $R_0 = 2.716\text{ \AA}$  agrees very well with the  $R_e = 2.717\text{ \AA}$  equilibrium separation determined from the MP2/aug-cc-

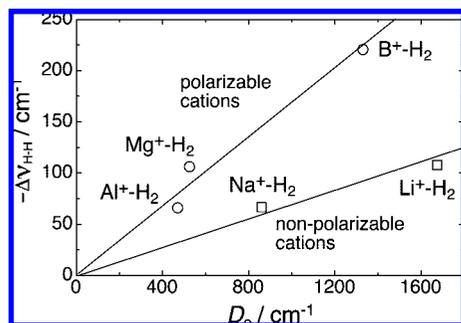
pVTZ calculations (see Figure 1). To some extent, the agreement is probably fortuitous as one would expect the vibrationally averaged intermolecular separation to exceed slightly the equilibrium separation. In contrast, the MP2(full)/6-31G\* level calculations described in ref 22 severely overestimate the intermolecular bond length (by  $0.8\text{ \AA}$ ) and underestimate the intermolecular stretch frequency (by  $\sim 120\text{ cm}^{-1}$ ). Apparently, the 6-31G\* basis set is too small to provide an adequate structural description of  $\text{Mg}^+-\text{H}_2$ . Despite this, the MP2(full)/6-31G\* binding energy ( $D_0 = 485\text{ cm}^{-1}$ ) agrees reasonably well with the MP2/aug-cc-pVTZ and CASSCF values ( $D_0 = 416$  and  $525\text{ cm}^{-1}$ , respectively).

The  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  spectra furnish little direct information on the frequencies of the intermolecular stretch and bend vibrational modes ( $\nu_s$  and  $\nu_b$ ) as the  $\nu_{\text{HH}} + \nu_s$  and  $\nu_{\text{HH}} + \nu_b$  combination bands have not been observed. However, the harmonic intermolecular stretch frequency of  $\text{Mg}^+-\text{H}_2$ , estimated from the  $\bar{B}$  and  $\Delta_J$  rotational constants ( $\omega_s = 193\text{ cm}^{-1}$ ), is close to the calculated MP2/aug-cc-pVTZ value ( $184\text{ cm}^{-1}$ ). For  $\text{Mg}^+-\text{D}_2$ , the harmonic intermolecular stretch frequency estimated from  $\bar{B}$  and  $\Delta_J$  is  $153\text{ cm}^{-1}$ . In a pseudodiatomic approximation the  $\omega_s$  values for  $\text{Mg}^+-\text{D}_2$  and  $\text{Mg}^+-\text{H}_2$  should have a ratio of 0.73, which is close to the ratio estimated from the spectroscopic constants (0.79).

The bending mode harmonic frequencies derived from MP2/aug-cc-pVTZ and CASSCF calculations are similar ( $436$  and  $410\text{ cm}^{-1}$ , respectively). However, the actual bending frequency is certainly somewhat lower considering that the barrier for internal rotation of the  $\text{H}_2$  subunit is only  $380\text{ cm}^{-1}$  (at the MP2/aug-cc-pVTZ level). Ultimately, a more comprehensive understanding of the large-amplitude intermolecular vibrations of  $\text{Mg}^+-\text{H}_2$  must await rovibrational energy level calculations using a full three-dimensional potential energy surface. These calculations will also allow a more rigorous comparison between the measured and computed rotational constants for the  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  complexes.

**4.2. Vibrational Predissociation Dynamics.** The observed IR transitions of  $\text{Mg}^+-\text{H}_2$  access quasibound  $n_{\text{HH}} = 1$  levels that are coupled to the  $\text{Mg}^+-\text{H}_2$  ( $n_{\text{HH}} = 0$ ) continuum. In principle, the vibrational predissociation rate can be extracted from the widths of the individual rovibrational lines. Broadening due to unresolved spin-rotation structure is expected to be negligible compared to the band width of the excitation light. Several of the more intense  $\text{Mg}^+-\text{H}_2$   $K_a = 1-1$  lines were used to estimate the lifetime broadening by fitting them to a Voigt profile with the full width half-maximum of the Gaussian component fixed to  $0.017\text{ cm}^{-1}$  (the bandwidth of the OPO IR radiation). The width of the resulting Lorentzian component is  $0.045 \pm 0.005\text{ cm}^{-1}$ , corresponding to an upper state lifetime of  $\tau_{\text{vp}} = 120\text{ ps}$ . For  $\text{Mg}^+-\text{D}_2$ , the width of the Lorentzian component for several of the more intense  $K_a = 0-0$  lines is  $0.030 \pm 0.002\text{ cm}^{-1}$ , corresponding to an upper state lifetime of  $\tau_{\text{vp}} = 180\text{ ps}$ . These  $\tau_{\text{vp}}$  values should be taken as provisional lower limits as the lines may be power broadened or Doppler broadened due to the ions having a spread of energy in the octopole region where they overlap with IR radiation. It should be noted that using the same instrument we have observed narrower, laser-limited transitions for  $\text{Br}^+-\text{D}_2$  and  $\text{I}^+-\text{D}_2$ .<sup>32,33</sup>

**4.3. Comparisons with Related Complexes.** It is interesting to compare the properties of  $\text{Mg}^+-\text{H}_2$  and other similar metal cation- $\text{H}_2$  complexes. As expected, the intermolecular bond length of  $\text{Mg}^+-\text{H}_2$  ( $2.716\text{ \AA}$ ) exceeds that of  $\text{Na}^+-\text{H}_2$  ( $2.493\text{ \AA}$ ) but is less than that of  $\text{Al}^+-\text{H}_2$  ( $3.035\text{ \AA}$ ); the bond length ordering reflects the Pauli repulsion between the  $\text{H}_2$   $\sigma_g$  orbital



**Figure 4.** H–H stretch vibrational frequency shift ( $-\Delta\nu_{\text{HH}}$ ) plotted against dissociation energy ( $D_0$ ) for  $\text{Li}^+-\text{H}_2$ ,  $\text{B}^+-\text{H}_2$ ,  $\text{Na}^+-\text{H}_2$ ,  $\text{Mg}^+-\text{H}_2$ , and  $\text{Al}^+-\text{H}_2$ . Trendlines are shown for complexes containing polarizable metal cations (○) and nonpolarizable metal cations (□). The plotted data are experimental values apart from the  $D_0$  values of  $\text{Li}^+-\text{H}_2$  and  $\text{Mg}^+-\text{H}_2$ , which are calculated values taken from refs 40 and 24, respectively.

and the half-filled and filled 3 s orbital in  $\text{Mg}^+$  and  $\text{Al}^+$ , respectively.<sup>34</sup> Similarly, one might anticipate that the binding energy of  $\text{Mg}^+-\text{H}_2$  should be bracketed by the binding energies of  $\text{Na}^+-\text{H}_2$  and  $\text{Al}^+-\text{H}_2$  (measured as 860 and 470  $\text{cm}^{-1}$ , respectively; refs 35 and 36). Direct comparisons are difficult because the binding energy of  $\text{Mg}^+-\text{H}_2$  has not been measured. The calculated MP2/aug-cc-pVTZ  $\text{Mg}^+-\text{H}_2$  binding energy ( $D_0 = 420 \text{ cm}^{-1}$ ) lies below the expected range, although it should be noted that this computational approach tends to underestimate the dissociation energies of  $\text{M}^+-\text{H}_2$  complexes by 100–200  $\text{cm}^{-1}$ .<sup>35–37</sup> The CASSCF calculations of Bauschlicher predict a somewhat higher binding energy (525  $\text{cm}^{-1}$ ), according better with expectations.<sup>24</sup>

The  $\nu_{\text{HH}}$  red-shift for complexes containing  $\text{H}_2$  is often presumed to be connected directly with the dissociation energy.<sup>38,39</sup> From this perspective, it is interesting to compare the vibrational red-shift ( $\Delta\nu_{\text{HH}}$ ) and binding energy ( $D_0$ ) for  $\text{Mg}^+-\text{H}_2$  with those of the  $\text{Li}^+-\text{H}_2$ ,  $\text{Na}^+-\text{H}_2$ ,  $\text{B}^+-\text{H}_2$ , and  $\text{Al}^+-\text{H}_2$  complexes which have also been characterized spectroscopically.<sup>10</sup> Interestingly, when  $\Delta\nu_{\text{HH}}$  is plotted against  $D_0$  (see Figure 4), the data for complexes containing cations with a half-filled or filled valence s orbital ( $\text{B}^+$ ,  $\text{Mg}^+$ ,  $\text{Al}^+$ ) and the data for complexes containing alkali metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ) lie on two separate lines. Generally, complexes containing the polarizable  $\text{B}^+$ ,  $\text{Mg}^+$ , and  $\text{Al}^+$  cations exhibit a larger  $\nu_{\text{HH}}$  red-shift for a given dissociation energy than complexes containing the nonpolarizable  $\text{Li}^+$  and  $\text{Na}^+$  cations. The differences are highlighted by comparing  $\text{Mg}^+-\text{H}_2$  and  $\text{Li}^+-\text{H}_2$ . The  $\Delta\nu_{\text{HH}}$  value for  $\text{Mg}^+-\text{H}_2$  ( $-106.2 \text{ cm}^{-1}$ ) is similar to that of  $\text{Li}^+-\text{H}_2$  ( $-107.8 \text{ cm}^{-1}$ ) yet  $\text{Mg}^+-\text{H}_2$  has a much lower dissociation energy (525  $\text{cm}^{-1}$  compared to 1675  $\text{cm}^{-1}$ ; refs 24 and 40) and a considerably longer intermolecular bond (2.703 Å compared to 2.056 Å; ref 8).

Reasons for the larger than expected red-shifts for complexes containing metal cations with a single or doubly occupied valence s orbital were elaborated in our previous study of the  $\text{B}^+-\text{H}_2$  complex.<sup>10</sup> It was found that a small admixture of the  $\text{B}^+ 2 p_z$  orbital in the HOMO (primarily  $\text{B}^+ 2 s$  and  $\text{H}_2 \sigma_g$  in character) results in electron density transfer from the  $\text{H}_2 \sigma_g$  orbital (0.02 electrons) to the  $2 p_z$  orbital causing the pronounced reduction of the  $\nu_{\text{HH}}$  frequency (i.e., a large red-shift). Involvement of the  $2 p_z$  orbital is promoted by polarization of the valence 2 s orbital away from the  $\text{H}_2$  molecule by electrons in the  $\sigma_g$  orbital. A similar effect is likely to occur for  $\text{Mg}^+-\text{H}_2$  (with transfer from the  $\sigma_g$  bonding orbital to the  $\text{Mg}^+ 3 p_z$  orbital). In contrast, for  $\text{Li}^+-\text{H}_2$  and  $\text{Na}^+-\text{H}_2$  complexes, the

alkali metal's unoccupied s and p orbitals lie much higher in energy and do not effectively hybridize with the  $\sigma_g$  orbital.

Polarization of the filled or half-filled valence s orbital of a metal cation by attached ligands plays an important role in deciding the structures of the larger  $\text{M}^+-\text{(H}_2)_n$  complexes. The  $\text{B}^+-\text{(H}_2)_2$ ,  $\text{Al}^+-\text{(H}_2)_2$ , and  $\text{Mg}^+-\text{(H}_2)_2$  species are all predicted to have bent structures; two  $\text{H}_2$  ligands positioned on the same side of the metal ion can concertedly polarize the cation allowing their closer approach to the positively charged core.<sup>34,36,41</sup> In contrast, the  $\text{Li}^+-\text{(H}_2)_2$  and  $\text{Na}^+-\text{(H}_2)_2$  species are predicted to be linear, with the two  $\text{H}_2$  ligands attached to opposite sides of the metal cation, a configuration that reduces ligand–ligand repulsion.<sup>8,34</sup>

## 5. Conclusions

The main outcomes of this work can be summarized as follows:

(1) Rotationally resolved IR spectra are obtained for  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  in the H–H and D–D stretch regions, respectively. Band centers for the  $\nu_{\text{HH}}$  and  $\nu_{\text{DD}}$  transitions of  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$  are red-shifted by 106.2 and 76.0  $\text{cm}^{-1}$ , respectively, from the stretch fundamentals of the free  $\text{H}_2$  and  $\text{D}_2$  molecules.

(2) The  $\text{Mg}^+-\text{H}_2$  complex has a T-shaped equilibrium structure with a vibrationally averaged  $\text{Mg}^+\cdots\text{H}_2$  separation of 2.716 Å, decreasing by 0.037 Å when the  $\text{H}_2$  subunit is vibrationally excited. The  $\text{Mg}^+-\text{D}_2$  complex has a similar vibrationally averaged intermolecular separation (2.687 Å), which decreases upon  $\text{D}_2$  vibrational excitation by 0.026 Å.

3. Lower limits for the predissociation lifetimes, estimated from the transition line widths, are 120 and 180 ps for  $\text{Mg}^+-\text{H}_2$  and  $\text{Mg}^+-\text{D}_2$ , respectively.

It is clear that there is no simple, general relationship between vibrational red-shift and binding energy for the  $\text{M}^+-\text{H}_2$  complexes, although periodic trends are beginning to emerge. Apparently, a complex containing a metal cation with a half-filled or filled valence s orbital has a larger  $\nu_{\text{HH}}$  red-shift than a complex containing an alkali metal cation with a comparable dissociation energy.

Ultimately, a more comprehensive understanding of the floppy  $\text{Mg}^+-\text{H}_2$  complex should be obtainable by calculating a full three-dimensional PES and using this to compute rovibrational energies that can be compared directly with spectroscopic transition energies. These calculations should also give reliable estimates for the dissociation energy and frequencies for the intermolecular vibrational modes.

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**Supporting Information Available:** Transition wavenumbers and assignments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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