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Photofragmentation Spectroscopy of MgD_2^+ L. N. Ding,[†] M. A. Young,[‡] P. D. Kleiber,[†] and W. C. Stwalley^{*,†,‡}

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MgD_2^+ ion–molecule complexes, produced in a liquid-nitrogen-cooled laser vaporization source, are mass-selected and studied by laser photofragmentation spectroscopy in a reflection time-of-flight mass spectrometer. We have observed molecular absorption to the red of the $\text{Mg}^+(3^2\text{S}_{1/2} - 3^2\text{P}_J)$ atomic resonance lines. Notably, the reactive daughter ion (MgD^+) is the only fragmentation product clearly observed in this spectral region. The molecular absorption profile consists of a seven-membered progression of discrete vibrational transitions with decreasing vibrational spacings from 489 to 314 cm^{-1} , superimposed on a broad continuum background. The observed spectrum can be tentatively assigned to the perpendicular transitions $1^2\text{B}_2, 1^2\text{B}_1 \leftarrow 1^2\text{A}_1$ in C_{2v} geometry. We assign the continuum background to the $1^2\text{B}_2 \leftarrow 1^2\text{A}_1$ transition. It is likely that reaction on this surface, possibly through insertion into a near linear $\text{D-Mg}^+-\text{D}$ intermediate, is direct and rapid. The presence of sharp, discrete vibrational absorption bands in the reactive fragmentation channel suggests a second, indirect reaction mechanism through a relatively long-lived excited-state complex. We assign this structure to the $1^2\text{B}_1 \leftarrow 1^2\text{A}_1$ transition. Presumably, reaction occurs indirectly through coupling to the 1^2B_2 state. The discrete structure within a given vibrational band is assigned to K subband rotational transitions ($K_a'' = 0 \rightarrow K_a' = 1$ and $K_a'' = 1 \rightarrow K_a' = 0, 2$) in *o*- and *p*- MgD_2^+ , respectively. Additional unassigned lines may be due to overlapping hot band absorptions or transitions from higher K_a'' states. An alternative spectral assignment based on excited-state spin–orbit fine structure is also noted.

Introduction

The field of cluster ion spectroscopy has undergone a rapid expansion as new and different (and frequently exotic) species are examined by novel experimental methods.^{1–14} The spectroscopic analysis of isolated molecular clusters provides a unique and powerful way to study the interactions important in condensed phases. For instance, many ion–molecule reactions proceed through a state of the reagents which may be weakly bound by noncovalent forces, corresponding to a local minimum on the reaction coordinate. If these species can be formed and isolated, then a photochemical reaction can be studied as a unimolecular process. Spectroscopic methods can be applied to partly reveal the shape of the potential energy surfaces for the reaction, and in cases where the excited-state complex is long-lived, specific vibrational degrees of freedom may be excited, yielding precise information on the complex structure. By monitoring both reactive and nonreactive fragmentation channels, information on the reaction mechanism can be obtained, including the complex lifetime and the effect of reagent electronic orbital alignment in the complex on the reaction dynamics.^{14–16}

In this work, we report preliminary studies of the chemical reaction and photofragmentation of isolated MgD_2^+ ion–molecule complexes. ($^{24}\text{MgD}_2^+$ was chosen over $^{24}\text{MgH}_2^+$ for reasons of experimental convenience in assigning the mass spectrum.) MgD_2^+ complexes are formed in a liquid-nitrogen-cooled laser vaporization source. The weakly bound complexes are mass-selected and studied by laser photodissociation spectroscopy in a reflection time-of-flight mass spectrometer (RTOFMS).¹¹ We have observed reproducible molecular absorption bands to the red of the $\text{Mg}^+(3^2\text{S}_{1/2} - 3^2\text{P}_J)$ resonance transitions in the spectral region from 280 to 315 nm. In this spectral range, $^{24}\text{MgD}^+$ is the only fragment daughter ion clearly observed. The reactive channel action spectrum shows a discrete vibrational resonance

structure superimposed on a broad continuum background, suggesting two reaction mechanisms: a direct (rapid) and an indirect (slow) pathway. Analysis of the vibrational resonance structure gives excited-state $\Delta G(v')$ values. We are also able to resolve excited-state splittings which we tentatively assign to the K subband structure. The experimental results are in reasonable agreement with recent theoretical predictions.^{17,18}

Experimental Section

The laser vaporization source is similar to that used to produce transition-metal clusters with rare-gas adducts¹² but modified to include a liquid-nitrogen-cooled extension channel. The supersonic expansion is initiated by a carrier gas pulse of neat D_2 from a commercial pulsed supersonic valve (10 Hz, 60- μs duration, R. M. Jordan Co.) operated at a backing pressure of 60 psi. The gas pulse flows through a narrow (1-mm-diameter) channel, around the Mg target rod, and then passes through a copper extension channel (1.5-mm diameter, 1.3-cm length). The extension channel is in thermal contact with a liquid nitrogen reservoir and thermally insulated from the source block by a nylon spacer; it has a typical operating temperature of 108 ± 2 K in these experiments (limited by the thermal conductivity of the insulating spacer).

The second harmonic of a pulsed Nd:YAG laser (Quanta Ray DCR11, 10-mJ energy in a 7-ns pulse) counterpropagates along the flow axis and is focused through the flow channel to a 500- μm spot on the Mg target rod at the flow centerline. The ablation laser pulse is timed to hit the rod near the middle of the carrier gas pulse.

Downstream from the nozzle (4–5 cm), the molecular beam passes through a 5-mm-diameter skimmer (Beam Dynamics Inc.) which separates the differentially pumped source chamber from the extraction chamber. The source chamber is pumped by a 10-in. diffusion pump and operates at a background pressure of 2×10^{-5} Torr. The extraction region is pumped by an LN2

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trapped 6-in. diffusion pump at a typical operating pressure of 5×10^{-6} Torr. Ions are pulse-extracted at right angles into a differentially pumped drift chamber which houses the reflectron assembly. A 300 L/s turbo pump maintains a typical operating pressure of 1×10^{-6} Torr in the flight tube.

The ion extraction plates are located ≈ 15 cm downstream from the skimmer, and the extraction and acceleration voltages are adjusted to achieve Wiley–McLaren space-focusing conditions.¹⁹ The extraction voltage, 250 V, is generated by a homemade fast switch with a 20-ns rise time and 0.4–2.5- μ s adjustable pulse duration. The second stage acceleration voltage of 1275 V yields a typical beam voltage of 1.4 keV. The RTOFMS is a modified version of a commercial instrument (R. M. Jordan Co.); the flight tube, accelerator, and ion optics are shielded and isolated from ground so that they can be floated at the acceleration voltage. Deflection voltages determine the angle of the ion trajectory with respect to the center axis of the flight tube. In our apparatus, this angle is about 6° .

Ions are mass-selected with a pulsed mass gate and focused into the reflectron by a three-element Einzel lens. Because the mass gate is close to the acceleration region, it has limited mass resolution (~ 5 amu FWHM in this mass region).

A tunable, frequency-doubled pulsed dye laser (Quanta Ray DCR2A/PDL2/WEX) is time-delayed to excite the “target” parent ion at the turning point in the reflectron.¹¹ The timing delays and triggering sequences are generated by a four-channel digital delay generator (Stanford Research Systems SRS Model DG-535). The laser is admitted into the reflectron assembly through narrow slits in one of the reflectron plates and intersects the ion beam in the plane of the beam path.

Parent and daughter ions are reaccelerated back into the flight tube and detected by a 40-mm microchannel plate detector. A digital oscilloscope (LeCroy 9400) is used to monitor the mass spectrum. The detector output is split to two gated integrators (Stanford Research Systems Model SRS 250); one monitors the parent ion signal, while the second monitors the daughter ion signal (after preamplification by a factor of 25). A third gated integrator is used to monitor the UV probe laser pulse energy which varies appreciably over the broad tuning range studied in this experiment. The three integrated and averaged output signals are collected with a personal computer. The photodissociation action spectrum is obtained by normalizing the MgD^+ daughter ion signal by the parent ion signal and probe laser intensity as a function of probe laser wavelength. The wavelength range covered (280–315 nm) lies to the red of the $\text{Mg}^+(3^2\text{S}_{1/2}-3^2\text{P}_{1/2})$ resonance and spans five laser dyes (Exciton DCM, R640, Kiton 620, R610, R590). The spectrum is collected in segments, and the different segments are pieced together by normalizing the spectra at the overlapping edges of the dye ranges.

In the present work, we have clearly observed and identified only the reactive fragmentation product, $^{24}\text{MgD}^+$. It is important to note that the flight time of the fragmentation product ions (in this case MgD^+ at mass 26) is different from the flight time of any ion from the source (for example, $^{26}\text{Mg}^+$ which is certainly present in the source) (Figure 1). The reason for this is that the fragmentation products have the same flight time as the parent (MgD_2^+ mass 28) from the extraction region to the reflectron and as the daughter (MgD^+ mass 26) from the reflectron to the final detector. This is important because it means we may precisely identify and measure the fragmentation product ion signal despite the presence of many other ions from the source in this mass region (which may be transmitted through our limited mass gate).

The major impurities at the parent mass 28 will be $^{25}\text{MgHD}^+$ and $^{26}\text{MgH}_2^+$ due to hydrogen impurity in the deuterium source. Analysis of the mass spectrum gives an upper limit for these impurities of $\leq 3\%$. (Note that the peak at mass 27 in Figure 1 is predominantly Al^+ impurity from the source block.) Assuming

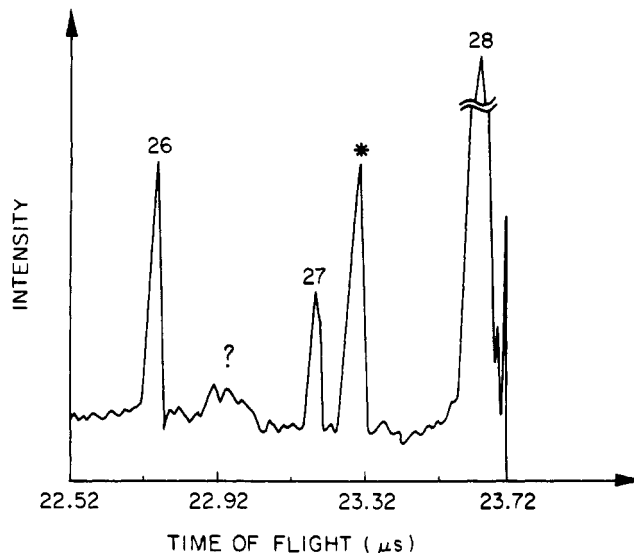


Figure 1. Molecular-ion mass spectrum. The numbered peaks correspond to molecular ions of masses 26–28 present in the source and transmitted through the mass gate: Mass 26 is predominantly $^{26}\text{Mg}^+$, mass 27 is $^{27}\text{Al}^+$ impurity from our source block, and mass 28 is the parent ion $^{24}\text{MgD}_2^+$. The peak marked with an asterisk is the reactive photofragmentation product $^{24}\text{MgD}^+$. The ? defines the expected position of the nonreactive fragmentation product $^{24}\text{Mg}^+$.

the hydrogenated compounds will fragment with similar efficiency, any contribution from these impurities in the spectrum would be too small to observe given our limited experimental signal-to-noise ratio.

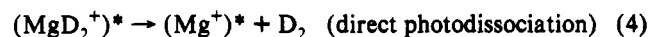
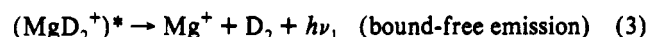
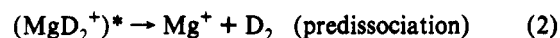
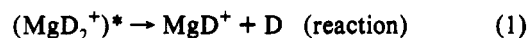
Our sensitivity was limited by the presence of strong mass peaks nearby the weak daughter ion peaks, which saturate the microchannel plate detector. This is a significant problem for the nonreactive $^{24}\text{Mg}^+$ daughter ion resulting from the fragmentation process, which arrives after the strong $^{26}\text{Mg}^+$ peak from the source. Therefore, although we did not clearly observe any nonreactive product, our sensitivity is limited and we cannot entirely rule out this product channel. We will correct this problem in future work with an improved mass gate.

Results and Discussion

The photofragmentation process may be schematically described as



followed by



In the spectral range to the red of the $\text{Mg}^+(3^2\text{S}_{1/2}-3^2\text{P}_j)$ resonance transitions covered in this work, the direct photodissociation channel (eq 4) is not energetically accessible by a single photon. As described above, we have definitively observed only the reaction channel (eq 1) in this spectral region. In Figure 2, we show the reactive photodissociation spectrum, i.e., the normalized $^{24}\text{MgD}^+$ daughter ion signal as a function of probe laser wavelength from 315 to 280 nm.

Remarkably, the reactive channel shows significant structure in the action spectrum. The spectrum consists of a broad

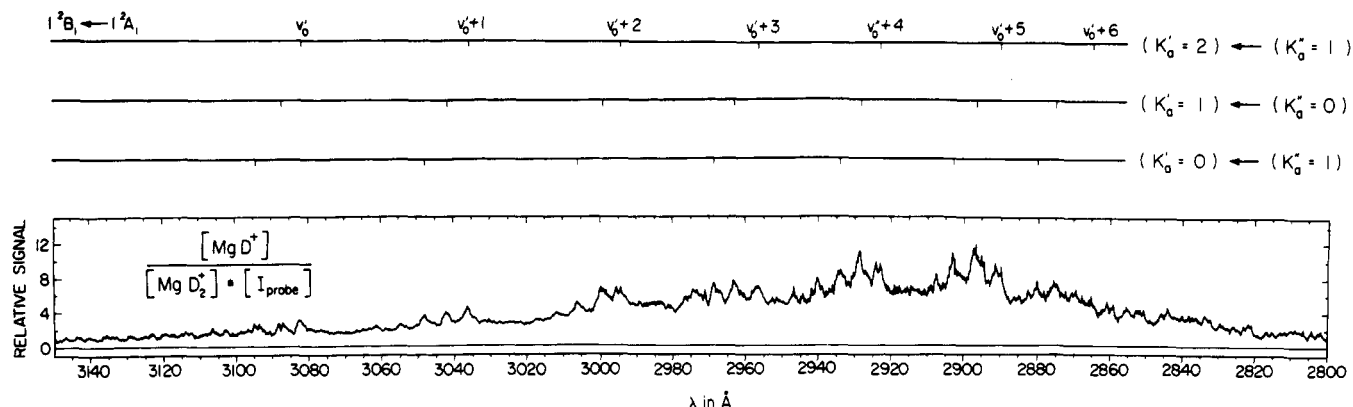


Figure 2. Reactive channel action spectrum showing the normalized $^{24}\text{MgD}^+$ daughter ion as a function of probe laser wavelength. Also shown is our tentative spectral assignment.

continuum with overlapping sharp discrete resonances showing a clear vibrational progression (Figure 2). Two-photon excitation of higher lying states of the MgD_2^+ complex is difficult to rule out entirely. The observed MgD^+ product signals are linear in laser power. For the continuum, this certainly indicates a one-photon process. However, it is easy to saturate a bound-bound transition, making such linearity tests somewhat less conclusive for the discrete structure. Nevertheless, our observations are consistent with a linear, one-photon process for both the continuum and the discrete structure in the spectrum.

We tentatively assign the observed molecular spectrum to the perpendicular $1^2B_1, 1^2B_1 \leftarrow 1^2A_1$ electronic transitions in C_{2v} geometry. The band origins are not observed, apparently due to a large change in equilibrium geometry in the excited state. We assign the continuum background to the transition $1^2B_2 \leftarrow 1^2A_1$. Based on previous studies of reactions in other metal-atom- H_2 systems,^{15,16,20,21} and on the ab initio calculations of Bauschlicher on MgH_2^+ ,¹⁸ we propose that reaction on the $\text{MgD}_2^+(1^2B_2)$ surface can proceed directly and rapidly, probably through metal-ion insertion into a $\text{D-Mg}^+-\text{D}$ transition state.

Superimposed on this continuum background, we can clearly identify seven members of a vibrational progression in the excited state (designated $v_0, v_0 + 1, \dots, v_0' + 6$ in Figure 2), with decreasing spacings from 489 to 314 cm^{-1} . There is a distinct substructure within each member of the progression; this can be plausibly assigned to the K subband structure in the $1^2B_1 \leftarrow 1^2A_1$ perpendicular electronic excitation, due to rotational transitions $K_{a''} = 0 \rightarrow K_{a'} = 1$ in *o*- MgD_2^+ and $K_{a''} = 1 \rightarrow K_{a'} = 0, 2$ in *p*- MgD_2^+ , respectively. These resonances exhibit widths of $\geq 20 \text{ cm}^{-1}$, perhaps due to the unresolved *J*-rotational structure. However, no consistent shading of the bands which might give information regarding the rotational band contours is discernible within our signal-to-noise. The observed widths put a lower limit on the lifetime of these states of $\sim 0.3 \text{ ps}$. Given the observed vibrational frequency of $\sim 400 \text{ cm}^{-1}$ (vide infra), this corresponds to an intermediate-state lifetime greater than ~ 3 vibrational periods. Furthermore, the bound-free indirect photodissociation channel (eq 3) has a lifetime of $\sim 3 \text{ ns}$ (the bare Mg^+ resonance fluorescence lifetime). Since no nonreactive Mg^+ product is observed (assuming a sensitivity comparable to that observed for MgD^+), we can also put an upper limit of $\leq 1 \text{ ns}$ on the excited complex lifetime. This indirect reaction mechanism may occur through weak coupling of the 1^2B_1 state to the 1^2B_2 state.

The $\Delta G_{v'+1/2}$ values for the observed vibrational bands are given in Figure 3. On the basis of our tentative assignment of the K subband structure, we can estimate values (A'' and A') for the *a*-axis rotational constants in the ground (1^2A_1) and excited (1^2B_1) states, respectively. The *a* axis corresponds to the C_2 symmetry axis, i.e., to the axis of the minimum moment of inertia. The experimental values are $A'' = 34 \pm 4 \text{ cm}^{-1}$ and $A' = 32 \pm 4 \text{ cm}^{-1}$, both in reasonable agreement with the theoretical predictions discussed below.

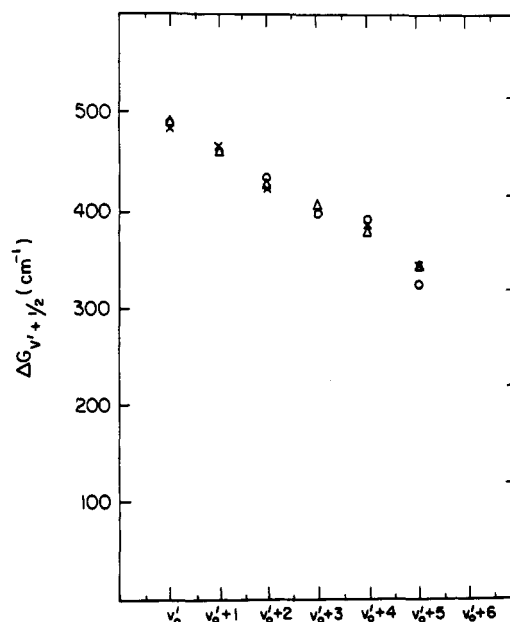


Figure 3. $\Delta G_{v'+1/2}$ plot for the observed vibrational progressions assigned to $1^2B_1 \leftarrow 1^2A_1$. The circles are from $K_{a''} = 1 \rightarrow K_{a'} = 2$, the crosses are from $K_{a''} = 0 \rightarrow K_{a'} = 1$, and the triangles are from $K_{a''} = 1 \rightarrow K_{a'} = 0$.

Theoretical calculations by Bauschlicher¹⁸ show that the Mg^+-H_2 ion-molecule complex is bound in a T-shaped geometry in the ground state (1^2A_1) with $D_e = 770 \text{ cm}^{-1}$ and an Mg^+-H_2 bond midpoint equilibrium separation of $R = 5.145a_0$. The H_2 bond length in the complex is $1.414a_0$, very close to the relaxed value of $1.401a_0$ in the isolated H_2 molecule. It is also important to note that the H_2 is probably not freely rotating. Calculations suggest the energy required to rotate the H_2 molecule from C_{2v} to linear geometry within the complex is $\sim 300 \text{ cm}^{-1}$,¹⁷ requiring a rotational temperature $\geq 400 \text{ K}$ which is unlikely for our supersonic molecular beam source. These theoretical calculations also give a Mg^+-H_2 intermolecular symmetric stretch (α_1) vibrational frequency of $\omega_e'' = 180 \text{ cm}^{-1}$. The reduced mass-scaled value for Mg^+-D_2 is $\omega_e'' = 132 \text{ cm}^{-1}$. For the theoretical equilibrium geometry, we calculate the *a*-axis rotational constant to be $A'' = 30.0 \text{ cm}^{-1}$, to be compared with the observed value $A'' = 34 \pm 4 \text{ cm}^{-1}$.

Bauschlicher has also carried out calculations on the MgH_2^+ excited states ($1^2B_1, 1^2B_2, 2^2A_1$) in the same C_{2v} symmetry. The 1^2B_1 state has a repulsive interaction at short distance, with a well depth of $D_e = 6440 \text{ cm}^{-1}$ and a minimum at $R = 3.664a_0$. Again the equilibrium H_2 bond length ($r = 1.447a_0$) is close to the isolated H_2 value. In contrast, the 1^2B_2 state is much more strongly bound, showing insertion of the Mg^+ into the H_2 bond to form a $\text{H-Mg}^+-\text{H}$ species with $R = 2.567a_0$, a bond angle of 81.7° ,

and a significantly greater H–H distance ($r = 4.441a_0$). The ab initio results for the 1^2B_2 state support the suggestion that the continuum absorption in the reactive action spectrum may result from direct excitation of the chemically active 1^2B_2 surface in C_{2v} geometry, followed by direct reaction through an insertion mechanism.

In the well of the long-range 1^2B_1 state, the theoretical value for the intermolecular Mg^+H_2 symmetric stretch vibrational frequency is $\omega_e' = 802\text{ cm}^{-1}$. For Mg^+D_2 , the corresponding value is 588 cm^{-1} , which is quite consistent with the observed range of $\Delta G_{v+1/2}$ values, from 489 to 314 cm^{-1} , given a reasonable anharmonicity. In fact, if we assume this theoretical value of 588 cm^{-1} for $\Delta G_{1/2}$ in the 1^2B_1 state, we can extrapolate our Birge–Sponer plot back to the intercept and estimate $v_0 = 4 \pm 1$ and an excited-state binding energy $D_e \sim 5000 \pm 600\text{ cm}^{-1}$. This is to be compared with the theoretical $D_e = 6440\text{ cm}^{-1}$ for the 2^2B_1 state. From the slope of the $\Delta G_{v+1/2}$ plot, we may also estimate $\omega_e x_e = 14\text{ cm}^{-1}$. The theoretical equilibrium geometry in the 1^2B_1 state implies an excited-state rotational constant $A' \approx 29.3\text{ cm}^{-1}$, to be compared with the observed value of $32 \pm 4\text{ cm}^{-1}$.

We stress that these assignments are tentative. There are reproducible unassigned peaks which, while somewhat smaller than the structure we have identified, are not negligibly small. These may result from overlapping hot band absorption or transitions from higher K_a'' states. They might also result from two-photon excitation of higher electronically excited states. The presence of an additional stable geometry (e.g., linear) would also complicate the spectrum, although there is no evidence for a secondary minimum on the ground-state surface from the theoretical calculations.

Peak intensities of the assigned features should be roughly in the ratio 2:1 for the $K_a'' = 0:K_a'' = 1$ transitions based on the expected ortho/para ratio for MgD_2^+ . This assumes that the room-temperature value is “frozen” during the supersonic expansion and that there is negligible ortho–para interconversion. Our signal-to-noise is not sufficient to demonstrate this ratio reproducibly in each vibrational band, although it appears to approximately hold.

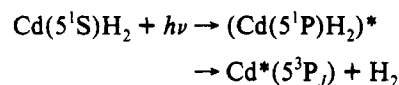
It is also important to note that the spectral assignment is further complicated by the fact that the spin–orbit interaction in the complex will probably be $\sim 60\text{ cm}^{-1}$ in magnitude,^{13,14} leading to splittings roughly the same as the predicted K subband spacing. In addition, the ground-state vibrational spacing, $\omega_e'' = 132\text{ cm}^{-1}$, is roughly twice the predicted K subband splitting. Thus, the observed splittings of $\sim 60\text{ cm}^{-1}$ could also be interpreted as resulting from a combination of spin–orbit splitting and hot band absorption, in a pseudodiatom $A^2\Pi \leftarrow X^2\Sigma^+$ transition. However, this seems less likely given the fairly strong binding and anisotropy in the ground state and the large 2^2B_2 – 2^2B_1 potential splittings in the excited state.

We have also observed the photofragmentation of MgD_2^+ when the probe laser is fixed at 266 nm (using the fourth harmonic of the Nd:YAG laser), to the blue of the $Mg^+(3^2S\text{--}3^2P)$ resonance lines. In this case, we presumably excite the complex to the repulsive 2^2A_1 surface; interestingly, here we observe only the nonreactive channel, Mg^+ .

It is worthwhile to compare our general observation with results from previous work on similar systems. In studies of the photodissociation spectrum of neutral $Hg\text{--}H_2$ van der Waals complexes, Breckenridge et al.¹⁵ observed a broad structureless action spectrum leading to the HgH reaction product when the probe laser was tuned to the attractive “ Π -like” excited state of the complex on the red wing of the $Hg(6^1S_0\text{--}6^3P_1)$ intercombination line. Lack of discernible structure suggested the reaction was direct and that the transition state was short-lived. The authors proposed that the reaction proceeds on the attractive surface in C_{2v} geometry through insertion into a H–Hg–H

transition state. Similar arguments have been given for other neutral metal atom– H_2 reactions as well.^{20,21} When the probe laser was tuned to the blue of the Hg resonance, exciting the repulsive “ Σ^+ -like” state of the complex, a vibrational structure in the reactive action spectrum was observed, indicative of a relatively long-lived intermediate. Indeed, it was suggested that reaction in this case might proceed only through a weak coupling to the “ Π ” state.¹⁵

Breckenridge and co-workers have also studied nonreactive quenching in the photodissociation of CdH_2 ,¹⁶



The red-wing action spectrum for the $Cd^*(5^3P_J)$ quenching channel is similar in some respects to our MgD_2^+ reactive action spectrum. It exhibits a broad continuum indicative of a direct and rapid predissociation via a surface crossing between the attractive $CdH_2^*(5^1P(1^1B_2))$ level in C_{2v} geometry and the lower lying 3^1A_1 and 3^1B_1 surfaces correlating to the $Cd^*(5^3P_J)$ manifold. However, superimposed on this continuum is a series of sharp vibrational resonances. The discrete resonances are tentatively assigned to perpendicular transitions ($1^1B_1; K_a' = 0$) \leftarrow ($1^1A_1; K_a'' = 1$) in $o\text{-}CdH_2$; the ($1^1B_1; K_a' = 0$) states are apparently quite long-lived and couple only weakly to the dissociative 1^1B_2 states of CdH_2 . Presumably the other ($1^1B_1; K_a' > 0$) states couple very efficiently to the 1^1B_2 surface and, hence, do not lead to any discernible resonance structure.

Duncan and co-workers have studied the photofragmentation spectra of $Mg^+\text{--}CO_2$ ion–molecule complexes using techniques essentially similar to those described here.^{13,14} When the laser is tuned to the red of the Mg^+ resonance lines, they find only the nonreactive product Mg^+ presumably formed through channels analogous to (2) and (3) above or through resonant two-photon excitation of higher states. A discrete bound-state resonance structure is observed and explained in terms of the spin–orbit structure in the linear complex. (Incidentally, to test our system, we have repeated and verified these observations). When the laser is tuned to the blue of the Mg^+ resonance, however, both reactive and nonreactive daughter product ions are detected. In this case, the action spectrum for the reactive channel is a broad structureless continuum, again suggesting a rapid direct reaction mechanism.^{13,14}

More recently, Duncan and co-workers have extended these measurements to $Mg^+\text{--}H_2O/D_2O$ complexes.²² In the spectral region studied (to the red of the Mg^+ resonance line), only the nonreactive product, Mg^+ , was observed. The spectrum was highly structured and was assigned to electronic transitions $2^2B_2, 2^2B_1 \leftarrow X^2A_1$. Vibrational bands involving both stretching and bending in the van der Waals mode were observed. Analysis of the partially resolved K subband structure supported the conclusion that the complex has a C_{2v} equilibrium structure.

Conclusion

MgD_2^+ ion–molecule complexes, produced in a liquid-nitrogen-cooled laser vaporization source, were mass-selected and studied by laser photofragmentation spectroscopy in a reflection time-of-flight mass spectrometer. We observed molecular absorption to the red of the $Mg^+(3^2S_{1/2}\text{--}3^2P_J)$ atomic resonance lines. Notably the reactive daughter ion (MgD^+) was the only fragmentation product clearly observed in this spectral region. The molecular absorption profile consists of a seven-membered progression of discrete vibrational transitions with decreasing vibrational spacings from 489 to 314 cm^{-1} , superimposed on a broad continuum background. The observed spectrum has been tentatively assigned to the perpendicular transitions $1^2B_2, 1^2B_1 \leftarrow 1^2A_1$ in C_{2v} geometry. We assign the continuum background to the transition $1^2B_2 \leftarrow 1^2A_1$. It is likely that reaction on this

surface, possibly through insertion into a near linear $\text{D-Mg}^+-\text{D}$ intermediate, is direct and rapid. The presence of sharp discrete vibrational absorption bands in the reactive fragmentation channel suggests a second, indirect reaction mechanism through a relatively long-lived excited-state complex. We assign this structure to the $1^2\text{B}_1 \leftarrow 1^2\text{A}_1$ transition. Presumably, reaction occurs indirectly through coupling to the 1^2B_2 state. A discrete structure within a given vibrational band was assigned to the rotational transitions $K_a'' = 0 \rightarrow K_a' = 1$ and $K_a'' = 1 \rightarrow K_a' = 0, 2$ in *o*- and *p*- MgD_2^+ , respectively. Additional unassigned lines may be due to overlapping hot band absorption or transitions from higher K_a'' states. An alternative spectral assignment based on the excited-state spin-orbit fine structure has also been noted.

In future work, we will install an improved mass gate to allow greater sensitivity in the detection of the photofragment ions. We will further study blue-wing absorption to the $\text{B}^2\Sigma^+-\text{like}$ excited state of the complex, carry out isotopic substitution experiments to verify the absolute vibrational numbering in the excited state, carry out higher resolution studies of the observed vibrational resonances to check for rotational structure, and give a more complete and quantitative comparison with theoretical model predictions.

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