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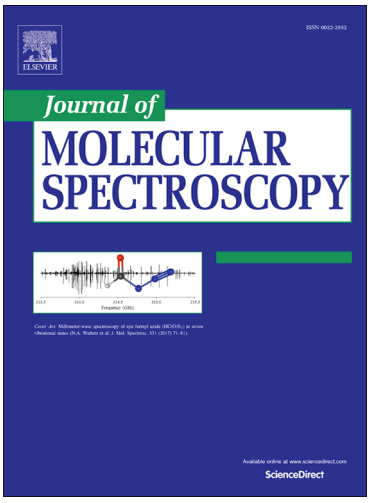

Pulsed-laser spectroscopy of the highly excited $C\ ^2$ and $1\ ^2$ states of MgH

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Pulsed-laser spectroscopy of the highly excited $C\ ^2\Pi$ and $1\ ^2\Delta$ states of MgH

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Abstract

We present the results of laser-ablation molecular jet experiments on the high-lying $C\ ^2\Pi$ and $1\ ^2\Delta$ electronic states of MgH, obtained via laser-induced fluorescence with frequency-doubled pulsed laser beams and with a visible-visible double resonance technique. The $C\ ^2\Pi$ state is examined for the first time in nearly 50 years. The $1\ ^2\Delta$ state was last reported in 1937, when it was misassigned as the $D\ ^2\Sigma^-$ state. These two states are fit with a modern standard Hamiltonian. Finally, measurements of the lifetime of the F_2 $J = 1.5$ f level in the $v = 0$ $A\ ^2\Pi$ state are reported; lifetimes of levels of the $C\ ^2\Pi$ state were very short (less than the 10 ns lower limit available in our experiment).

Keywords: magnesium hydride, ultraviolet spectrum, double resonance spectroscopy, frequency doubling

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1. Introduction

MgH has been the subject of extensive investigation from the ultraviolet to the microwave regions since the molecule's first spectral identification in 1878[1]. Observations include pure-rotational far-infrared transitions within the $v = 0$ and $v = 1$ levels of the ground electronic state $X\ ^2\Sigma^+$[2–4], the infrared rotation-vibration spectrum[5, 6], and electronic spectra in the visible involving the low-lying $B'\ ^2\Sigma^+$ and $A\ ^2\Pi$ electronic states in transition to the $X\ ^2\Sigma^+$ state (see refs. [7–9] and the references therein for a comprehensive overview of previous work). Data providing information about $X\ ^2\Sigma^+$ are very extensive, and include a wide variety of levels from v=0 to near dissociation for several isotopologues; consequently, a potential curve of impressive accuracy has been determined by direct potential fitting[7, 9]. These studies have been partially motivated by the astrophysical significance of MgH, the spectra of which have been observed against sunspots, and from type M stars. These observations have allowed for determination of the surface gravity of some stars, based on relative isotopic abundances deduced from MgH features.[10, 11]

Most of the more recent work on MgH has focused on the lowest-lying electronic states $X\ ^2\Sigma^+$, $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$, which are accessible with Fourier transform, laser, and microwave techniques. However, prior to the 1980s much of the work on this species was done on grating instruments equipped with photographic plates, which were more suitable for recording spectra from the green-visible to the ultraviolet. A number of electronic states lying between 35000-43000 cm^{-1} above $X\ ^2\Sigma^+$ were observed in this manner.[12–

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21]

The electronic structure of MgH has been investigated theoretically over the full range of observed states, most recently by Mestdagh *et al.*[22] and by Guitou *et al.*[23]. The theoretical work provides a consistent framework for interpretation of the experimental results, and includes important information regarding the rotational couplings and the transition moments between different states. The calculations also provide a guide and roadmap for experimentalists, who can anticipate what to expect in a particular investigation.

The work we report on here began during a search for another magnesium-bearing molecule, $MgOCH_3$. While taking survey spectra in a laser-ablation molecular jet source, we found strong transitions arising from the 0-0 band of the $A\ ^2\Pi - X\ ^2\Sigma^+$ system of MgH. The spectra were rotationally resolved even with our pulsed laser system, and this led us to consider two-photon double resonance experiments using individual rotational levels of the $A\ ^2\Pi$ state as an intermediate to access higher-lying electronic states. In addition, we had equipment suitable for doubling the laser frequency into the ultraviolet, and could attempt to access some of the highly excited states directly from the ground state. We first focused on the $C\ ^2\Pi$ state, which makes strong transitions to $X\ ^2\Sigma^+$ at 243 nm, and to $A\ ^2\Pi$ at 455 nm. After successfully collecting and analyzing the spectra taken both directly and with double resonance, we explored other excited states accessible to our apparatus. In the process, we have been able to reassign a spectrum reported in 1937[24], thereby clarifying an inconsistency in the assignment of the upper state, and identifying it with a state predicted by theory, but absent in the current lists of experimentally observed electronic states.

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2. Experimental

MgH molecules were created in the pulsed laser-ablation source at the University of New Brunswick. Atoms were ablated under vacuum from a magnesium rod 1/4 inch in diameter with 10 mJ pulses of laser light 355 nm in wavelength and 10 ns in duration, provided by a tripled Nd:YAG laser. The rod was continuously rotated and translated to ensure even ablation over its surface. The release of a pulse of gas (methanol diluted to 1% in helium, delivered at a plenum pressure of 40 psi) was timed so that the gas passed through the cloud of magnesium atoms and expanded supersonically through a circular channel 2 mm in diameter and 7 mm long into the high vacuum of $\sim 10^{-5}$ Torr created in the experimental chamber by a large diffusion pump. To acquire spectra of MgH, pulsed, tuneable laser beams ($\sim$0.1 cm^{-1} bandwidth) from Nd:YAG-pumped dye lasers were passed through the chamber at right angles to the jet about 5 cm below the orifice at the end of the circular channel to excite the molecules entrained in the gas pulse. The resulting laser-induced fluorescence (LIF) was collected perpendicular to both the jet and the laser beam by a slitless Jarrell-Ash monochromator 0.25 m in focal length, which served as a tunable bandpass filter. A Hamamatsu R-928 photomultiplier tube mounted at the exit of the monochromator detected the LIF, and the resulting electrical signal was amplified, and then was processed either by a boxcar integrator or a Stanford Research Systems SR400 photon counter. The dye laser beam's wavenumber was calibrated by picking off a small portion of its intensity with a glass plate and directing it into an argon-filled uranium hollow cathode lamp, from which optogalvanic signals from atomic Ar and U transitions were obtained. The uranium line positions

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were compared to values from the atlas[25] of Palmer *et al.* To ensure that the dye laser frequency scan was linear, a second pick-off beam was sometimes expanded and directed into an etalon with a free spectral range of 0.25 cm^{-1}. The intensity of the central portion of the output bull's-eye diffraction pattern was detected with a silicon photodiode.

Spectra of MgH were obtained with two different techniques: one-photon ultraviolet LIF spectroscopy, and two-photon LIF spectroscopy in which visible photons from one dye laser beam pumped an intermediate level of the $A\ ^2\Pi$ state while a beam from a second, independent laser excited the molecule to a higher state. The light for the one-photon spectra was obtained by doubling the wavenumber of the visible dye laser light in a BBO crystal mounted in a Lumonics HyperTRAK-1000 system, which synchronized the angle-tuned phase matching of the primary and doubled beams with the laser scan. To acquire the two-photon spectra, the triggerings of the Nd:YAG lasers pumping the dye lasers were synchronized in time with a Stanford Research Systems SR535 delay generator so that the beams passed through the experimental chamber at about the same time, such that the signal levels were maximized. In either case, the light beams entering the experimental chamber had energies of 2-3 mJ per pulse, spread over 10-20 ns. The one- and two-photon spectra we obtained are provided as supplementary data to this paper; for analysis the data were smoothed with a 5-7 point boxcar filter, and all figures presented here were processed in this manner.

We also measured the lifetimes of some excited states of MgH by tuning one dye laser's wavenumber to a transition, then recording the time evolution of the unprocessed signal from the photomultiplier on a Tektronix TDS 524A

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2-channel oscilloscope with a bandwidth of 500 MHz. The temporal waveform was averaged for 100 pulses with the laser exciting the LIF released and again with it blocked. The two waveforms were then subtracted to remove electrical artifacts present in the signal, and the resulting waveform was fit to an exponential function to determine its time constant.

3. Data and analysis

3.1. Studies of the $C\ ^2\Pi$ state of MgH

The $C\ ^2\Pi - X\ ^2\Sigma^+$ spectrum near 243 nm was first reported in 1909[26], but to our knowledge the present study is the first since 1970[20], and the first to be conducted with laser spectroscopy. We obtained LIF spectra both by exciting the $C\ ^2\Pi - X\ ^2\Sigma^+$ transitions directly with ultraviolet photons, and by exciting $A\ ^2\Pi - X\ ^2\Sigma^+$ then $C\ ^2\Pi - A\ ^2\Pi$ transitions with two near-simultaneous visible photons. For the one-photon experiments, fluorescence from the $C\ ^2\Pi - A\ ^2\Pi$ 0-0 band was detected, while for the two-photon spectra the 0-1 band was monitored. In both cases, the fluorescence was far enough from the laser wavelength(s) so that laser scatter was virtually eliminated due to the finite bandpass of the filtering monochomator, greatly improving the signal-to-noise ratio of the spectra.

The $C\ ^2\Pi - X\ ^2\Sigma^+$ spectrum taken with one-photon LIF is shown in Fig. 1, and measurements of the spectral line positions and assignments are given in Table 1. The width of unblended, clearly resolved lines was $\sim$0.5-0.6 cm^{-1}, limited by Doppler broadening in our molecular jet. (Our pulsed beams strike a much larger volume of the expanding jet as compared to our cw laser beams, and thus sample a wider distribution of velocity components

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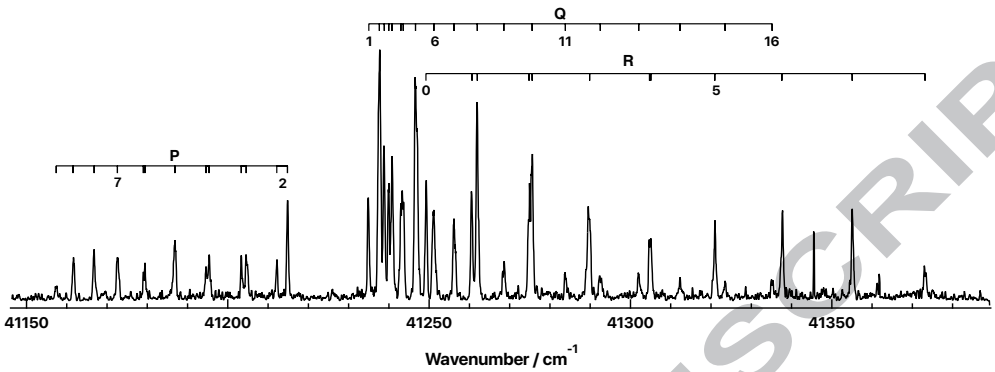

Figure 1: Single-photon pulsed laser scan of the 0-0 band in the $C\ ^2\Pi - X\ ^2\Sigma^+$ system of MgH using frequency-doubled UV laser light produced via second harmonic generation.

along the direction of the laser beam. With cw laser beams, we can achieve linewidths below 0.01 cm^{-1} in the same jet.) The predissociation in the R and P branches noted by previous investigators and discussed in Herzberg Vol. 1[27] and in Ref. [22] was evident in our data; we observed lines up to only R(8) and P(9), while in the Q branch lines up to Q(16) could be measured. The assignments were greatly aided by comparison with Balfour's photographic spectrum and line list[20]; however, there are structured and systematic differences between our measurements and Balfour's which result in discrepancies as large as ± 0.4 cm^{-1}. We used our 0.25 cm^{-1} etalon to confirm the linearity of our laser scans, and thus suspect that the differences result from small distortions in the photographed spectrum resulting from alignment of the grating spectrometer, developing the exposed plate, and measurement with the comparator apparatus.

These data were complemented by measurements from the two-photon experiments, for which seven levels from the F_1 component ($^2\Pi_{1/2}$) and six

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Table 1: Measured line positions in the one-photon $C\ ^2\Pi - X\ ^2\Sigma^+$ spectrum of MgH. Uncertainty in the transition wavenumbers is estimated at 0.15 cm^{-1}. The bracketed numbers are unresolved blends, for which we assign an uncertainty of 0.5 cm^{-1}. Note that the lines labeled $Q_{2e2f}(0.5)$ and $P_{2f2f}(1.5)$ should be labeled $Q_{1e2f}(0.5)$ and $P_{1f2f}(1.5)$ since all $J' = 0.5$ levels are properly in the F_1 manifold of the $C\ ^2\Pi$ state.

N''	$J''(e)$	$P_{1e1e}(N'')$	$Q_{1f1e}(N'')$	$R_{1e1e}(N'')$	$J''(f)$	$P_{2f2f}(N'')$	$Q_{2e2f}(N'')$	$R_{2f2f}(N'')$
0	0.5			41249.18				
1	1.5		41237.61	41261.95	0.5		41234.99	41260.64
2	2.5	41214.82	41238.83	41275.55	1.5	41212.13	41237.60	41274.76
3	3.5	41204.59	41240.79	(41289.80)	2.5	41203.35	41239.95	(41289.80)
4	4.5	41195.30	41243.55	(41304.95)	3.5	41194.63	41242.95	(41304.95)
5	5.5	(41186.82)	(41246.52)	41320.93	4.5	(41186.82)	(41246.52)	41320.93
6	6.5	(41179.40)	41251.49	41337.60	5.5	(41179.40)	41251.24	41337.60
7	7.5	41172.58	41256.19	41355.06	6.5	41172.58	41256.19	41355.06
8	8.5	41166.80	41261.95	41373.14	7.5	41166.80	41261.95	41373.14
9	9.5	41161.55	41268.51		8.5	41161.55	41268.51	
10	10.5		41275.57		9.5		41275.57	
11	11.5		41283.82		10.5		41283.82	
12	12.5		41292.50		11.5		41292.50	
13	13.5		41302.04		12.5		41302.04	
14	14.5		41312.30		13.5		41312.30	
15	15.5		41323.48		14.5		41323.48	
16	16.5		41335.17		15.5		41335.17	

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levels from the F_2 component ($^2\Pi_{3/2}$) of the $A\ ^2\Pi$ state were pumped with a first laser beam, while a second beam was tuned over all possible transitions of the $C\ ^2\Pi - A\ ^2\Pi$ 0-0 band arising from the pumped state. Levels from $J = 0.5$ to 3.5 in $A\ ^2\Pi$ were pumped, and each of these allowed up to six $C\ ^2\Pi - A\ ^2\Pi$ transitions to be measured without blending from transitions originating on a different lower level. Figure 2 contains examples of the spectra obtained from the two-photon experiment scans, in which the widths of strong, unblended lines was $\sim$0.4-0.45 cm^{-1}. We note that all expected $C\ ^2\Pi - A\ ^2\Pi$ lines arising from each of the $A\ ^2\Pi$ levels populated by the pumping laser appeared with a few interesting exceptions. Firstly, we saw no fluorescence from the $C\ ^2\Pi - A\ ^2\Pi$ $Q_{2e1f}(1.5)$ line when the $A\ ^2\Pi$ $F_1, J = 1.5$ f level was pumped, nor from the $Q_{2f1e}(1.5)$ line when the $A\ ^2\Pi$ $F_1, J = 1.5$ e level was pumped. Secondly, pumping the $F_2, J = 3.5$ e level of $A\ ^2\Pi$ produced no detectable $C\ ^2\Pi - A\ ^2\Pi$ transitions at all. These intensity anomalies are very likely to be associated with interactions between $C\ ^2\Pi$ and nearby states, since the $A\ ^2\Pi$ state $v = 0$ levels are quite isolated from other electronic states.

Term values for the $C\ ^2\Pi$ state were generated from the spectral lines by adding the term value of the lower state ($X\ ^2\Sigma^+$ for the one-photon spectrum or $A\ ^2\Pi$ for the double resonance experiments) taken from Ref. [8] to each of our transition energies. Since in many cases different two-photon spectra measured the same $C\ ^2\Pi$ energy level some statistical analysis could be performed on the results, which indicated that the uncertainty in term values measured with this technique is about 0.10 cm^{-1}. The slightly wider width of lines in the single-photon spectrum indicated that an uncertainty of 0.15 cm^{-1} was more appropriate for those data, and for term values arising from

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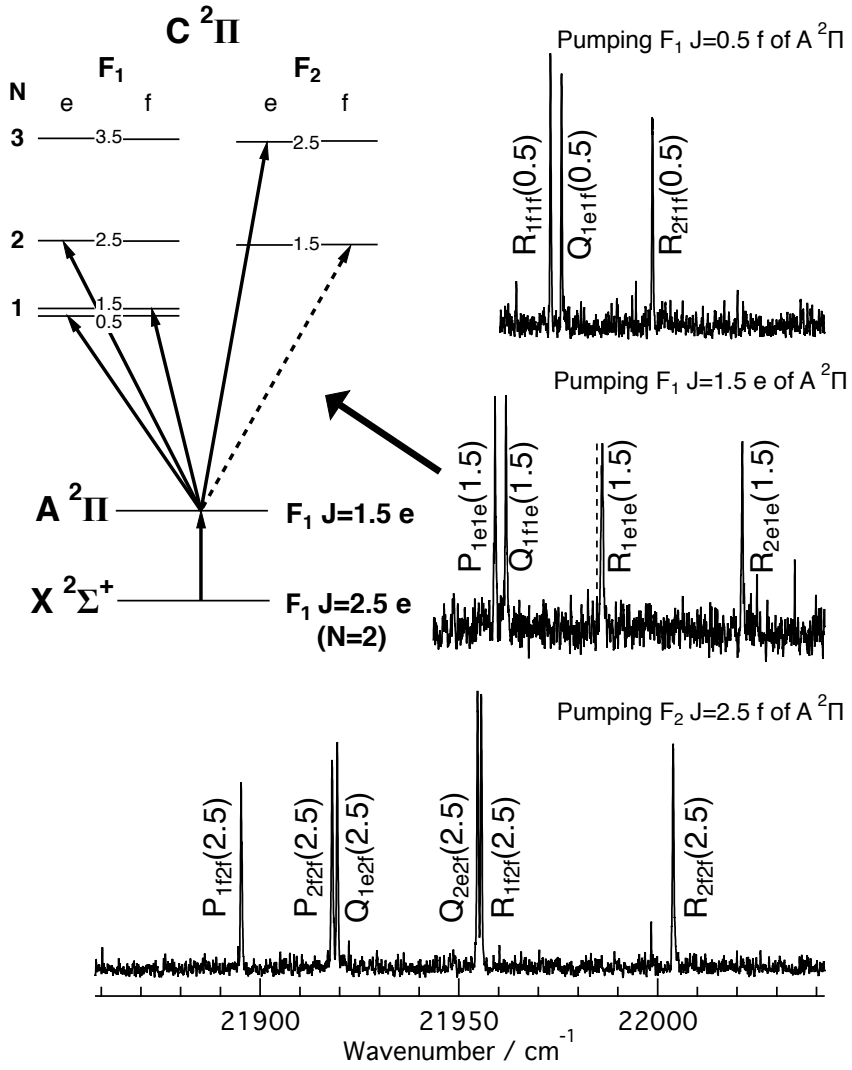

Figure 2: Two-photon scans of the $C\ ^2\Pi - A\ ^2\Pi$ 0-0 band of MgH. One laser is fixed and popluates a particular rotational level of the $A\ ^2\Pi$ state via the $A\ ^2\Pi - X\ ^2\Sigma^+$ transition, and a second laser excites all possible levels of the $C\ ^2\Pi - A\ ^2\Pi$ transition accessible from the pumped level. The spectra shown are taken in laser-induced fluorescence as a function of wavenumber of the second laser beam. The energy levels and transitions corresponding to the middle spectrum are shown in the inset. The dotted lines in the middle spectrum and energy diagram indicate a transition that was expected, but did not appear (see the text).

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Table 2: Results of fitting term values of the $C\ ^2\Pi$ state of MgH to a $^2\Pi$ Hamiltonian using PGOPHER[28]. Parameter values are given in cm^{-1}, and the 1σ statistical uncertainties in the last digits are given in parentheses after the value. Comparisons with parameters obtained in earlier work are given when available.

Parameter	Our Value	Previous Work
T_C	41242.292(13)	41242.5 [a]
A	3.821(55)	3.7 [b]
B	6.10533(53)	6.090 [a]
D	$3.210(32)\times10^{-4}$	3.1×10^{-4} [a]
q	0.02673(62)	

[a] Turner and Harris (1937) [15]

[b] Balfour (1970, 1980) [20], [21]

the P(5)/P(6), Q(5) and R(3)/R(4) lines, where the lines were broadened due to unresolved splitting, uncertainty of 0.5 cm^{-1} was used.

All measured term values, whether generated from one- or two-photon scans and including each independent measurement of a given term, were fit to a $^2\Pi$ Hamiltonian with the program PGOPHER[28]. Due to the modest resolution of the pulsed laser system only five parameters were required to characterize the $C\ ^2\Pi\ v = 0$ level: the vibronic term energy T_C, rotational constant B, centrifugal distortion constant D, spin-orbit parameter A and the Λ-type doubling parameter q. They are given in Table 2, along with their statistical uncertainties and with some results from previous studies. The input data set, PGOPHER file and the output of the fitting procedure are given as supplementary material to this paper.

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Table 3: Term values of the $C\ ^2\Pi$ state of MgH, calculated from the fit parameters given in Table 2.

N	J	$F_1\ e$	$F_1\ f$	J	$F_2\ e$	$F_2\ f$
0	0.5	41246.46	41246.51			
1	1.5	41249.26	41249.20			
2	2.5	41273.44	41273.28	1.5	41271.90	41272.06
3	3.5	41309.98	41309.66	2.5	41308.71	41309.03
4	4.5	41358.77	41358.23	3.5	41357.50	41358.04
5	5.5	41419.75	41418.95	4.5	41418.35	41419.15
6	6.5	41492.86	41491.74	5.5	41491.24	41492.36
7	7.5	41578.06	41576.57	6.5	41576.135	41577.63
8	8.5	41675.29	41673.37	7.5	41672.99	41674.91
9	9.5	41784.49	41782.08	8.5	41781.74	41784.13
10	10.5		41902.64	9.5	41902.33	
11	11.5		42034.95	10.5	42034.67	
12	12.5		42178.95	11.5	42178.69	
13	13.5		42334.52	12.5	42334.285	
14	14.5		42501.59	13.5	42501.36	
15	15.5		42680.02	14.5	42679.82	
16	16.5		42869.72	15.5	42869.53	

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3.2. The $1\ ^2\Delta$ *state*

Our success at studying the $C\ ^2\Pi$ state of MgH prompted us to consider experiments on other nearby states. We attempted to collect data from the $E\ ^2\Sigma^+$ state near 35550 cm^{-1}, but the laser-induced fluorescence spectrum using frequency-doubled laser pulses was very weak, and this was abandoned. Examining Herzberg and Huber's compendium of molecular constants[29] showed another possible candidate for study labeled $D\ ^2\Sigma^-$, near 42065 cm^{-1}. This state was identified by Guntsch, who analyzed the $D\ ^2\Sigma^- - A\ ^2\Pi$ transition near 22860 cm^{-1} in 1937[24]. However, an examination of recent theoretical studies[22, 23] revealed that no $^2\Sigma^-$ states exist in the vicinity of 42065 cm^{-1}. Instead, just above the $C\ ^2\Pi$ state is the $1\ ^2\Delta$ state, calculated to lie at 42790 cm^{-1} in one study and at 44253 cm^{-1} in the other. We supposed that the $D\ ^2\Sigma^-$ state was in fact really the $1\ ^2\Delta$ state from the theoretical work, and began its study.

The one-photon approach using frequency-doubled laser light was not available to us, since the $1\ ^2\Delta - X\ ^2\Sigma^+$ transition is forbidden. We instead attempted the two-photon experiment, again pumping individual rotational levels of $A\ ^2\Pi\ v = 0$ with the beam from one laser then exciting to levels of the $1\ ^2\Delta$ with a second beam. Guntsch's line list gave us direction as to where to search, but since our experiment restricts us to the lowest values of J in a given state there was little overlap between Guntsch's data and ours. Initially we set our monochomator to detect fluorescence directly back to levels of $A\ ^2\Pi\ v = 0$ and obtained a signal. However, fluorescence to other vibrational levels proved much weaker, and so our spectra were noisier than we had hoped (roughly a 3:1 signal-to-noise ratio) due to detection

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of laser scatter along with the signal. Further, some lines appeared in the scans with or without the initial pumping beam; they were clearly due to another species (possibly C_2, which we make easily in our source, excited by the second beam to fluoresce in the 2-0 or 3-1 bands of the Swan system). The lines from the other species could also be distinguished by noting that they appeared at the same position in the two-photon scans regardless of the v=0 $A\ ^2\Pi$ level that was pumped. Despite these limitations, we were able to measure the positions of all expected levels in the upper state from J=1.5 to 4.5. Examples of the data we obtained are given in Fig. 3, and the list of the transitions observed and term values generated for the $1\ ^2\Delta$ is provided in Table 4. At the resolution and low values of J available to us, neither Λ-type doubling nor spin-orbit coupling was evident. Accordingly, the data were fit with PGOPHER to only two parameters, the vibronic term energy T_Δ (= 42167.358(39) cm^{-1}) and rotational constant B (=6.2820(31) cm^{-1}). The rotational constant can be compared to the value 6.289 cm^{-1} given by Guntsch[24]. The $1\ ^2\Delta$ fitting is included in the same set of supplementary data as is provided for the $C\ ^2\Pi$ state.

3.3. Radiative lifetimes of the $A\ ^2\Pi$ state

We measured the lifetimes of specific rotational levels in the $v = 0$ manifold of the $A\ ^2\Pi$ and $C\ ^2\Pi$ states of MgH using the procedure described in Section 2. To check for systematic errors we first recorded the lifetimes of the $3s3p\ ^3P^o_{0,1,2}$ atomic states of Mg by monitoring the $3s3p\ ^3P^o_{0,1,2} - 3s4s\ ^3S_1$ atomic lines between 516-519 nm. The results we obtained were consistent between the three lines, and averaged to 12.5±0.2 ns, in good agreement with value of 11.5±1.0 ns given by Aldenius *et al.*[30] Their experiment had

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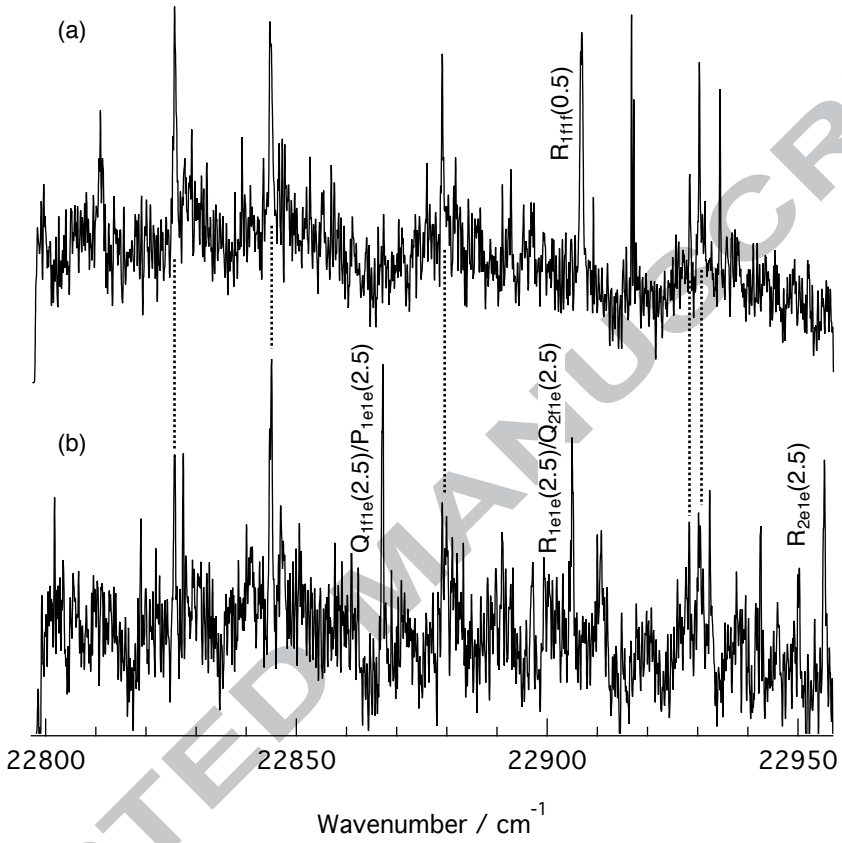

Figure 3: Two-photon scans of the 1 $^2\Delta - A\ ^2\Pi$ 0-0 band of MgH. One laser is fixed and populates a particular rotational level of the $A\ ^2\Pi$ state via the $A\ ^2\Pi - X\ ^2\Sigma^+$ transition, and a second laser is scanned to excite all possible levels of the 1 $^2\Delta - A\ ^2\Pi$ transition accessible from the pumped level. The spectra shown are taken in laser-induced fluorescence as a function of wavenumber of the second laser beam. Spectrum (a) arose from excitation of the $A\ ^2\Pi$ F_1 $J = 0.5$ f level with the pumping laser beam, from which only the one labelled 1 $^2\Delta - A\ ^2\Pi$ transition was possible. For spectrum (b) the F_1 $J = 2.5$ e level was pumped, and three transitions (two of which are unresolved doublets) were seen and are labelled. Dotted lines mark examples of lines from unknown species which appear regardless of whether the $A\ ^2\Pi$ pump laser is blocked or released.

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Table 4: Transitions in the $1\ ^2\Delta - A\ ^2\Pi$ 0-0 band observed in this work via double-resonance spectroscopy. In some cases a particular transition was observed more than once, and the multiple measurements have been averaged for this table. The data are also presented in the supplementary material to this paper, with each measurement individually reported on an energy level map and an associated spectrum. Uncertainties in these numbers are estimated at 0.10 cm^{-1}.

$A\ ^2\Pi - X\ ^2\Sigma^+$ transition	$A\ ^2\Pi$-state level	$1\ ^2\Delta$-state level	$1\ ^2\Delta - A\ ^2\Pi$ transition	transition wavenumber / cm^{-1}
$P_{1e1e}(1)$	F_1 0.5 e	F_1 1.5 e	$R_{1e1e}(0.5)$	22906.85
$P_{1e1e}(2)$	F_1 1.5 e	F_1 2.5 e / F_1 1.5 f	$R_{1e1e}(1.5)$ / $Q_{1f1e}(1.5)$	22892.75
$P_{1e1e}(2)$	F_1 1.5 e	F_2 2.5 e	$R_{2e1e}(1.5)$	22930.40
$R_{1e1e}(1)$	F_1 2.5 e	F_1 2.5 f / F_1 1.5 e	$Q_{1f1e}(2.5)$ / $P_{1e1e}(2.5)$	22867.15
$R_{1e1e}(1)$	F_1 2.5 e	F_1 3.5 e / F_2 2.5 f	$R_{1e1e}(2.5)$ / $Q_{2f1e}(2.5)$	22905.01
$R_{1e1e}(1)$	F_1 2.5 e	F_2 3.5 e	$R_{2e1e}(2.5)$	22955.22
$R_{1e1e}(2)$	F_1 3.5 e	F_1 3.5 f / F_2 2.5 e	$Q_{1f1e}(3.5)$ / $P_{2e1e}(3.5)$	22867.86
$R_{1e1e}(2)$	F_1 3.5 e	F_1 4.5 e / F_2 3.5 f	$R_{1e1e}(3.5)$ / $Q_{2f1e}(3.5)$	22918.26
$R_{1e1e}(2)$	F_1 3.5 e	F_2 4.5 e	$R_{2e1e}(3.5)$	22980.85
$Q_{1f1e}(0)$	F_1 0.5 f	F_1 1.5 f	$R_{1f1f}(0.5)$	22906.82
$Q_{1f1e}(1)$	F_1 1.5 f	F_1 2.5 f / F_1 1.5 e	$R_{1f1f}(1.5)$ / $Q_{1e1f}(1.5)$	22892.62
$Q_{1f1e}(1)$	F_1 1.5 f	F_2 2.5 f	$R_{2f1f}(1.5)$	22930.32
$Q_{1f1e}(2)$	F_1 2.5 f	F_1 2.5 e / F_1 1.5 f	$Q_{1e1f}(2.5)$ / $P_{1f1f}(2.5)$	22866.96
$Q_{1f1e}(2)$	F_1 2.5 f	F_1 3.5 f / F_2 2.5 e	$R_{1f1f}(2.5)$ / $Q_{2e1f}(2.5)$	22905.04
$Q_{1f1e}(2)$	F_1 2.5 f	F_2 3.5 f	$R_{2f1f}(2.5)$	22955.25
$Q_{1f1e}(3)$	F_1 3.5 f	F_1 2.5 f	$P_{1f1f}(3.5)$	22829.60
$Q_{1f1e}(3)$	F_1 3.5 f	F_1 3.5 e / F_2 2.5 f	$Q_{1e1f}(3.5)$ / $P_{2f1f}(3.5)$	22867.64
$Q_{1f1e}(3)$	F_1 3.5 f	F_1 3.5 e / F_2 2.5 f	$Q_{1e1f}(3.5)$ / $P_{2f1f}(3.5)$	22867.65
$Q_{1f1e}(3)$	F_1 3.5 f	F_1 4.5 f / F_2 3.5 e	$R_{1f1f}(3.5)$ / $Q_{2e1f}(3.5)$	22918.07
$Q_{1f1e}(3)$	F_1 3.5 f	F_1 4.5 f / F_2 3.5 e	$R_{1f1f}(3.5)$ / $Q_{2e1f}(3.5)$	22918.07
$Q_{1f1e}(3)$	F_1 3.5 f	F_2 4.5 f	$R_{2f1f}(3.5)$	22980.93
$R_{2e1e}(0)$	F_2 1.5 e	F_1 1.5 f / F_1 2.5 e	$Q_{1f2e}(1.5)$ / $R_{1e2e}(1.5)$	22861.31
$R_{2e1e}(0)$	F_2 1.5 e	F_2 2.5 e	$R_{2e2e}(1.5)$	22899.31
$R_{2e1e}(1)$	F_2 2.5 e	F_1 1.5 e / F_1 2.5 f	$P_{1e2e}(2.5)$ / $Q_{1f2e}(2.5)$	22825.75
$R_{2e1e}(1)$	F_2 2.5 e	F_2 2.5 f / F_1 3.5 e	$Q_{2f2e}(2.5)$ / $R_{1e2e}(2.5)$	22863.57
$R_{2e1e}(1)$	F_2 2.5 e	F_2 3.5 e	$R_{2e2e}(2.5)$	22914.04
$R_{2e1e}(2)$	F_2 3.5 e	F_2 4.5 e	$R_{2e2e}(3.5)$	22928.41
$R_{2f2f}(1)$	F_2 1.5 f	F_1 1.5 e / F_1 2.5 f	$Q_{1e2f}(1.5)$ / $R_{1f2f}(1.5)$	22861.34
$R_{2f2f}(1)$	F_2 1.5 f	F_2 2.5 f	$R_{2f2f}(1.5)$	22899.27
$R_{2f2f}(2)$	F_2 2.5 f	F_1 1.5 f / F_1 2.5 e	$P_{1f2f}(2.5)$ / $Q_{1e2f}(2.5)$	22825.81
$R_{2f2f}(2)$	F_2 2.5 f	F_2 2.5 e / F_1 3.5 f	$Q_{2e2f}(2.5)$ / $R_{1f2f}(2.5)$	22863.50
$R_{2f2f}(2)$	F_2 2.5 f	F_2 3.5 f	$R_{2f2f}(2.5)$	22913.90
$R_{2f2f}(3)$	F_2 3.5 f	F_2 3.5 e / F_1 4.5 f	$Q_{2e2f}(3.5)$ / $R_{1f2f}(3.5)$	22865.50
$R_{2f2f}(3)$	F_2 3.5 f	F_2 4.5 f	$R_{2f2f}(3.5)$	22928.24

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some possible complications due to collisionally-induced quenching and mixing that ours avoids by using a supersonic jet.

We excited the $R_{2f2f}(1)$ line of the 0-0 $A\ ^2\Pi - X\ ^2\Sigma^+$ transition with our pump laser, which allowed us to measure the F_2 $J = 1.5$ f rotational level of the $v = 0$ $A\ ^2\Pi$ state. Accounting for statistical uncertainty in the fitting to obtain the time constant, and for the scatter in a number of independent determinations, we obtained a value of 52.4±1.3 ns. We then attempted to measure rotational levels of the $v = 0$ $C\ ^2\Pi$ state via both the $C\ ^2\Pi - X\ ^2\Sigma^+$ and $C\ ^2\Pi - A\ ^2\Pi$ transitions, but they decayed very quickly, and we could only place an upper bound of 10 ns (the limit of our apparatus' capabilitiy) on their lifetimes. The signal-to-noise ratio we obtained from $1\ ^2\Delta - A\ ^2\Pi$ transitions was insufficient to permit measurement of $1\ ^2\Delta$ state lifetimes.

4. Discussion and conclusions

Our work on the $C\ ^2\Pi$ state of MgH has proven the viability of performing experiments on highly excited molecular states in our laboratory, either with frequency-doubled laser beams or with two-photon techniques. We have been able to obtain a rotational analysis using a modern $^2\Pi$ Hamiltonian, and the results are in good agreement with previous determinations of the vibronic term energy for the $v = 0$ level, the rotational constant and the centrifugal distortion constant. The spin-orbit constant A is conclusively shown to be positive; there was some confusion in this regard since it was given as negative in the original paper that measured it[20]; this was later amended to positive by the same author[21]. In any case, the weak spin-orbit effect means that the $C\ ^2\Pi$ state exhibits near-perfect Hund's case b angular momentum coupling.

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The Λ-doubling in a case b Π state of any spin multiplicity is expected to be given by $|\Delta\nu| = |q|N(N+1)$[31], and this is consistent with our result, which determines the Λ-doubling parameter q of $C\ ^2\Pi$ for the first time. The doubling is caused by interactions with $^2\Sigma^+$ states, the nearest of which are the experimentally observed $E\ ^2\Sigma^+$ and $F\ ^2\Sigma^+$ states[17] (labeled $3\ ^2\Sigma^+$ and $4\ ^2\Sigma^+$ in the calculations given in [22] and [23]), which lie below $C\ ^2\Pi$, and by the as-yet unobserved $5\ ^2\Sigma^+$ and $6\ ^2\Sigma^+$ states, which lie above $C\ ^2\Pi$. The parameter q for each $^2\Pi \sim^2 \Sigma^+$ interaction is given by Lefebvre-Brion and Field[32]:

$$q = \frac{2b^2B^2}{E_\Pi - E_\Sigma} \tag{1}$$

where B is the average rotational constant between the $^2\Pi$ and $^2\Sigma^+$ states, and the matrix element $b =< \pi|l^+|\sigma >$ for a situation in which the $^2\Pi$ state arises from a $(...)(\pi^1)$ electron configuration and the $^2\Sigma^+$ state from a $(...)(\sigma^1)$ configuration, with (...) representing a set of filled molecular orbitals. This is basically the situation in MgH, for which the $C\ ^2\Pi$ state arises from a $(...)(3\pi^1)$ configuration, and the four nearby $^2\Sigma^+$ states from mixtures of $(...)(n\sigma^1)$ configurations in the notation of Ref. [23].

Since q is greater than zero, the sum of the influences from $^2\Sigma^+$ states below $C\ ^2\Pi$ is stronger than the sum from those above. In a highly excited state like $C\ ^2\Pi$, it is unlikely that 'unique perturber' scenario is valid, but if one applies it here under all of the assumptions outlined in Ref. [32], then $b = \sqrt{l(l+1)} = \sqrt{2}$, and using the values for E_Π, B and q determined from our analysis we find that $E_\Pi - E_\Sigma \sim 5625$ cm^{-1}, so that $E_\Sigma \sim 35620$ cm^{-1}. Interestingly, this is very close to the experimentally determined energy of 35551 cm^{-1} for the $E\ ^2\Sigma^+$ state. Perhaps the interactions of the $F\ ^2\Sigma^+$,

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5 $^2\Sigma^+$ and 6 $^2\Sigma^+$ states with C $^2\Pi$ nearly cancel, leading to this result, or perhaps it is just a serendipitous artifact of the summation of all of the influences. Investigation of the spin splittings in these nearby $^2\Sigma^+$ states, which represent the other effect of the $^2\Pi \sim^2 \Sigma^+$ interaction, might shed some light on this situation.

We have clarified a longstanding issue with regard to the state reported for the first (and until now only) time as D $^2\Sigma^-$ in 1937; it is in fact the 1 $^2\Delta$ predicted in theoretical work. It lies at about 42170 cm^{-1}, a little lower than predicted either with pseudopotential theory[22] (42790 cm^{-1}) or with MRCI methods[23] (44250 cm^{-1}). The bond length that we calculate from the rotational constant B is 3.149 bohr, which can be compared to the theoretical values of 3.167 and 3.099 bohr. The spin-orbit splitting of this state is very small (beyond our ability to measure it), so for our purposes this is a Hund's case b $^2\Delta$ state.

Finally we have measured the lifetime of the F_2 $J = 1.5$ f level of the $v = 0$ manifold of the A $^2\Pi$ state. Our result of 52.4±1.3 ns, is somewhat higher than a previous measurement[33] of 43.6±3.0 ns, obtained by Nedelec and Dufayard in 1978[33], who employed a spectrally broader laser beam (∼0.3 Å) that excited several rotational lines (J ∼13.5-16.5) from both spin-orbit components at the same time, and who used a heated static cell for their experiment. Our experimental results can be compared to values of 40.5 and 41.5 ns deduced from theoretical transition probabilities obtained in 1971[34, 35]. More recent calculations from 2012 and 2013[36, 37] place a 46 ns lifetime on the level we have excited in our experiment.

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5. Acknowledgements

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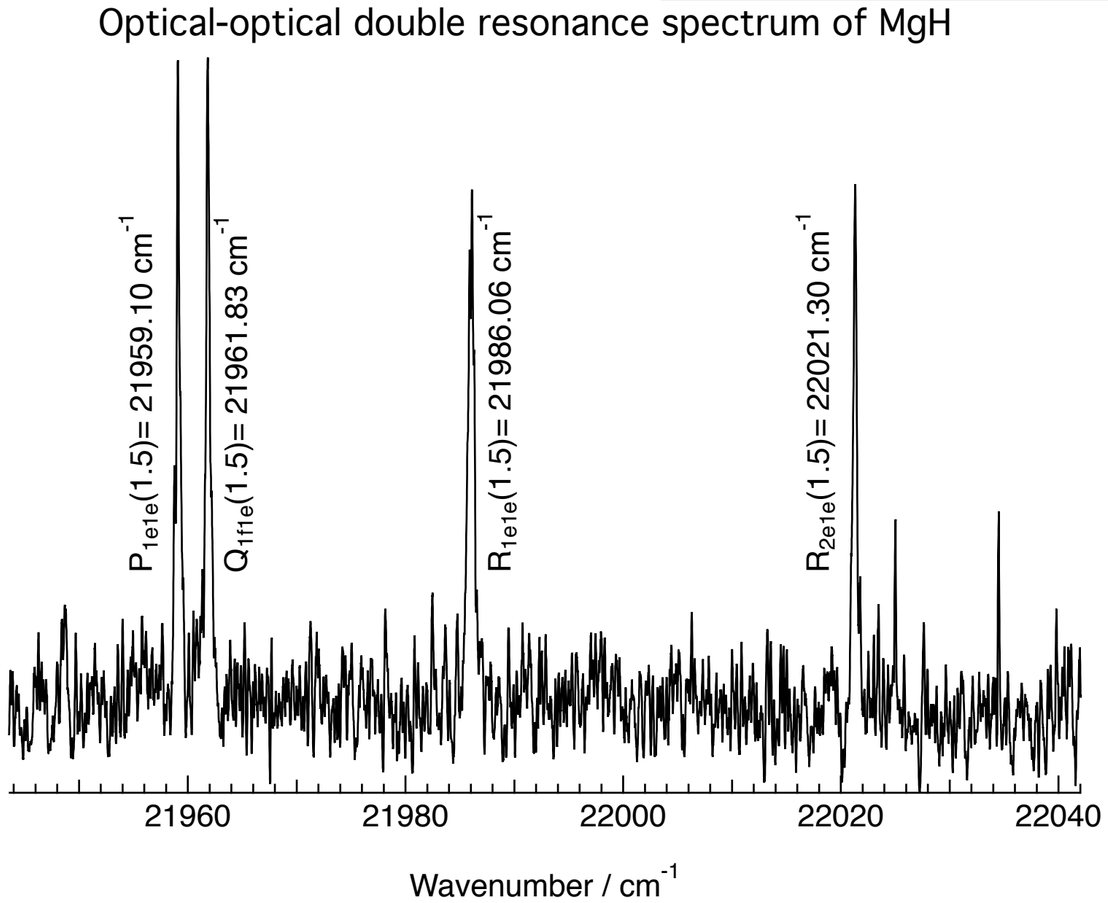
Optical-optical double resonance spectrum of MgH
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Q1f1e(1.5)= 21961.83 cm-1
R1e1e(1.5)= 21986.06 cm-1
R2e1e(1.5)= 22021.30 cm-1
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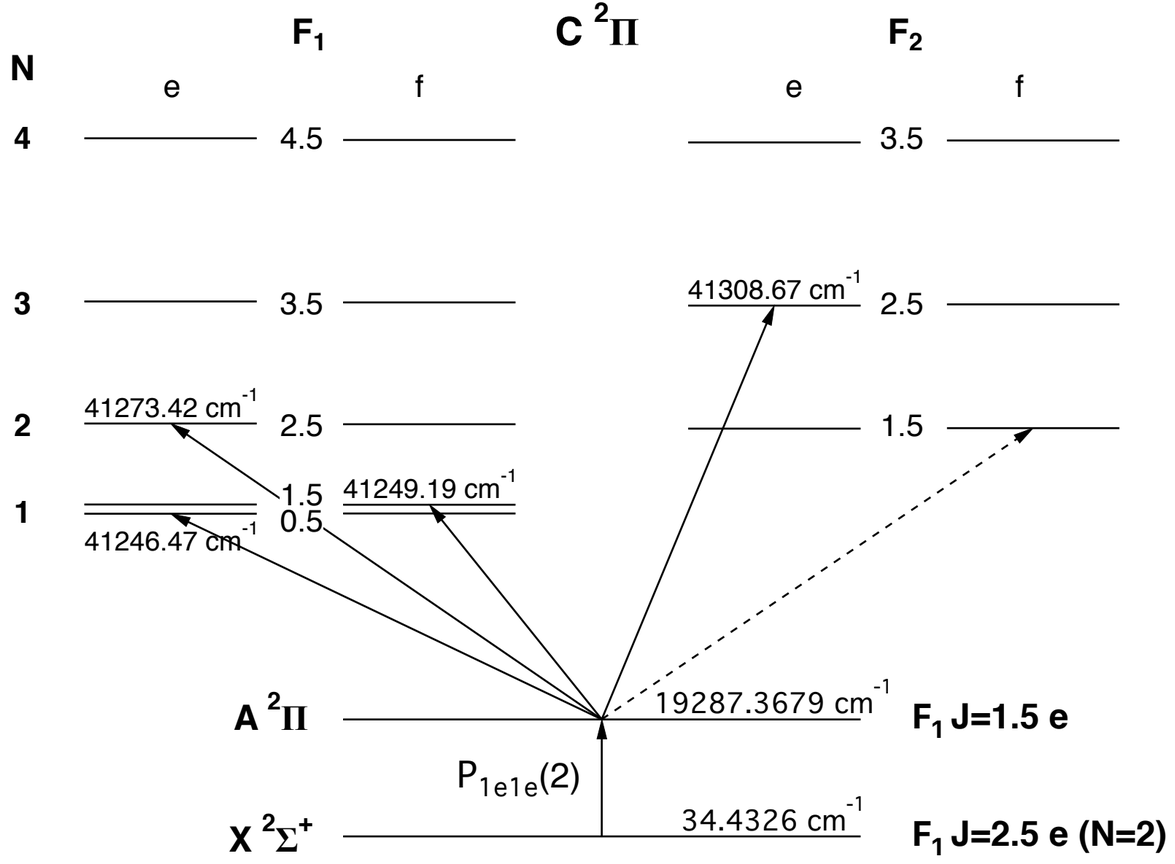
22000
22020
22040
Wavenumber / cm-1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C 2Π
F2
N
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f
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f
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4.5
3.5
3
3.5
2.5
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2
41273.42 cm-1
2.5
1.5
1
1.5
41249.19 cm-1
0.5
41246.47 cm-1
A 2Π
19287.3679 cm-1
F1 J=1.5 e
P1e1e(2)
X 2Σ+
34.4326 cm-1
F1 J=2.5 e (N=2)

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- MgH was made in a laser-ablation molecular jet
- Highly excited states were studied with single UV photons and two-photon techniques
- First observation of $C\ ^2\Pi$ state with laser techniques
- $1\ ^2\Delta$ state was observed and fit; had been misassigned as $D\ ^2\Sigma^-$ in 1937
- Lifetimes of some $A\ ^2\Pi$ levels were measured

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Pulsed-laser spectroscopy of the highly excited C 2 and 1 2 states of MgH

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