Line list for the MgF ground state

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Abstract

An extended Morse oscillator (EMO) potential function was obtained by fitting the observed laboratory vibration-rotation and pure rotational spectra of the 24MgF X2Σ+ ground state. The fitted potential reproduces the observed transitions within the observation uncertainties. With this EMO potential and an analytic dipole moment function, the ro-vibrational line positions were calculated using LeRoy’s dPotFit code [20]. The potential function used was an Expanded Morse Oscillator (EMO) similar to the work of Barton et al. [21] on NaCl and KCl. The ground state potential energy function was studied with ab initio computations [22] on NaCl and KCl.

1. Introduction

The MgF molecule has been investigated extensively with different experimental and theoretical approaches [1–13]. A rotational analysis of the A2Π−X2Σ+ electronic spectrum of MgF was performed by Barrow and Beale [1]; vibration-rotation lines for ν = 0–7 and N up to 87 were analyzed by Barber et al. [2] from an infrared emission spectrum; millimeter-wave transitions were observed by absorption spectroscopy by Anderson [3,4] for ν = 0–3, N from 2 to 12.

MgF is a potential astrophysical molecule [4,5]. Metal salts such as NaCl, AlCl and KCl have been detected in the circumstellar shell of the cool carbon star IRC +10216 [14]. The identification of magnesium compounds in IRC +10216 [15,16] demonstrated that there is enough magnesium in the gas phase to form simple molecules. The observation of AlF [5] in the same object suggests that other metal fluorides may be present as well. Thus, it is possible that MgF may be detectable in objects such as IRC +10216, particularly with millimeter arrays such as SMA and ALMA, which led to the detection of TiO and TiO2 in YY Canis Majoris [17]. MgO is also predicted to be present in the atmospheres of hot rocky super-Earth exoplanets [18] and MgF might also be present.

As an ion radical, MgF molecule is also of particular theoretical interest. Various ab initio calculations show that the molecule is very ionic near equilibrium, but as the bond distance increases there is a curve crossing and MgF is covalent at long range near dissociation [7–13]. The electron spin resonance measurements by Knight et al. [6] showed that the spin density on the F atom is less than 4%, which supports the ionic picture of the radical as Mg+1F. The unpaired electron is located almost exclusively on the metal atom. Very recently, it has been suggested that laser cooling and magneto-optical trapping of MgF is possible [13] using the A2Π−X2Σ+ transition.

The goal of the present work is to provide a MgF line list for the quantitative analysis and prediction of infrared spectra of hot MgF as found for example in exoplanets. The re-rotational line positions and line intensities) are obtained by direct solution of the nuclear motion Schrödinger equation using Le Roy’s computer program LEVEL [19] with an accurate empirical potential energy function. The potential energy function was obtained by fitting the pure rotation [3,4] and vibration-rotation [2] data using LeRoy’s dPotFit code [20]. The potential function used was an Expanded Morse Oscillator (EMO) similar to the work of Barton et al. [21] on NaCl and KCl.

The ground state potential energy function was studied with both ab initio and empirical approaches. The ab initio data were obtained to study the behavior over the full range the potential; the empirical potential was used to improve the accuracy of the predicted vibration-rotation transitions. All ab initio computations were performed with the Molpro2012 [23] package.

An experimental dipole moment is not available for MgF so had to be obtained from ab initio calculations. The calculated line intensities are very sensitive to the form of the dipole moment function and its derivatives [24]. Dipole moment functions from several different ab initio approaches were therefore tried...
2. EMO potential function

As for NaCl [22], the observed MgF line positions are reproduced using Le Roy’s EMO potential model [21], which can be expressed as

\[ V(r) = D_e[1 - e^{-\Delta E/(kT)}]^2 \]  

(1)

where

\[ \psi(r) = \sum_{i=0}^{N} \beta_i \psi_i(r, r_i) \]  

(2)

\[ \psi_i(r, r_i) = \frac{\rho_i^p - \rho_i^p}{\rho_i^p + \rho_i^p} \]  

(3)

\( D_e \) is the potential well depth and \( r_i \) is the equilibrium distance. \( N (=6) \) and \( p (=3) \) are preset parameters, and \( \beta_i \) are parameters determined using Le Roy’s dPotFit code [20]. \( D_e \) was fixed to a literature value and \( r_e \) was determined by the fit. The observed transitions used in the fit are summarized in Table 1.

\( D_e \) was set to 37297.24 cm\(^{-1}\), which was obtained using \( D_e = D_0 + E_0 \), with \( D_0 \) taken from Haynes [29], and the zero-point energy \( E_0 \) calculated from the spectroscopic constants of Barber et al. [2]. In total 763 observed transitions were fitted with a dimensionless standard error (DSE) of 1.026. The 2\(^{9}\)MgF pure rotation data were corrected for the effects of fine and hyperfine structure as in Barber et al. [2]. For the vibration-rotation lines, the uncertainties assigned in the original experimental work [2], in the range of 0.001 cm\(^{-1} \) – 0.005 cm\(^{-1} \), were used and for the millimeter-wave data [3, 4], an uncertainty of 9.3 \times 10^{-7} \text{ cm}^{-1} \) was adopted. These uncertainties correspond to one standard deviation. The small spin splitting and F hyperfine structure was not resolved in the vibration-rotation spectrum recorded at 0.01 cm\(^{-1} \) [2] resolution and MgF was treated as if the ground state has \( 1\Sigma^+ \) symmetry. In the present work we aim to provide a vibration-rotation line list so we follow Barber et al. [2] and ignore fine and hyperfine structure. The EMO potential parameters obtained from dPotFit are presented in Table 2 along with 95% confidence limits.

3. Ab initio potential and dipole moment function

3.1. ACPF potential and dipole moment

We found that the averaged coupled-pair functional (ACPF) approach [26, 27] with the correlation-consistent polarized valence 5-zeta (cc-pV5Z) basis set of Dunning and co-workers [30–33] gives a reliable potential with satisfactory parameters at the equilibrium bond length. The complete active space multi-configurational self-consistent field (CASSCF) [34, 35] wave function with the same electron configuration was taken as the reference in this ACPF calculation. All the core orbitals were frozen, and the active space of 14 orbitals (8a1, 3b1, 3b2) was used for 9 valence electrons in the calculations. A considerable number of trial calculations were carried out with basis sets that ranged from vdz (cc-pvdz) to av5z (aug-cc-pv5z) for Mg and from vdz to av6z for F for both ACPF and MRCI (multi-reference configuration interaction) methods although not all calculations were successful. The ACPF/cc-pV5Z calculation was selected based on the values of \( r_e, \omega_p \) and the shape of the dipole moment function.

The \( r_e \) from our ACPF calculation is 1.7452 \text{ Å} which was in excellent agreement with the experimental value, \( r_e = 1.7499 \text{ Å} \) [2]. The calculated dipole moment (3.004 D) at \( r_e \) from ACPF is close to literature values (2.86–3.13 D) from different \textit{ab initio} methods, which are listed in Table 3. We note our ACPF dipole moment is from an optimization computation, which is slightly different than the value obtained by a single point calculation at the experimental \( r_e \).

The ACPF potential curve is smooth and agrees well with the EMO curve over most of the potential well as shown in Fig. 1. The \textit{ab initio} points differ from the EMO potential from about 3 Å to 5 Å, which is far from the range of the observed data (\(< 6000 \text{ cm}^{-1} \) from the minimum). Fig. 1 suggests that the EMO potential may be reliable up to about 20000 cm\(^{-1} \) from the bottom of the potential well. Therefore, some transitions slightly above the observed data range can be reliably predicted from this EMO potential. At long range, the EMO potential is not satisfactory, but this is out of the scope of the present research.

The shape of the ACPF dipole moment function is smooth in the

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**Table 1**

<table>
<thead>
<tr>
<th>MgF</th>
<th>Transitions</th>
<th>Wavenumber range</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anderson et al. [3, 4]</td>
<td>( \Delta v = 0, \Delta N = +1 )</td>
<td>3.1–12.3 cm(^{-1} )</td>
<td>( 9.3 \times 10^{-7} \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>( v = 0–3, N \leq 12 )</td>
<td>580–762 cm(^{-1} )</td>
<td>0.001–0.005 cm(^{-1} )</td>
<td></td>
</tr>
<tr>
<td>Barber et al. [2]</td>
<td>( \Delta v = 1, \Delta N = \pm 1 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( v = 0–7, N \leq 87 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**Table 2**

EMO potential parameters for MgF ground state.

<table>
<thead>
<tr>
<th>MgF EMO (N=6, p=3)</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_e/(\text{cm}^{-1}) )</td>
<td>37297.24</td>
</tr>
<tr>
<td>( r_e/(\text{Å}) )</td>
<td>1.74992860871D+00</td>
</tr>
<tr>
<td>( \beta_0 )</td>
<td>1.478548128092D+00</td>
</tr>
<tr>
<td>( \beta_1 )</td>
<td>–2.525625987692D-01</td>
</tr>
<tr>
<td>( \beta_2 )</td>
<td>1.671472842379D-01</td>
</tr>
<tr>
<td>( \beta_3 )</td>
<td>4.191108679342D-02</td>
</tr>
<tr>
<td>( \beta_4 )</td>
<td>9.576638726358D-02</td>
</tr>
<tr>
<td>( \beta_5 )</td>
<td>1.125082555037D-01</td>
</tr>
<tr>
<td>( \beta_6 )</td>
<td>1.617929283888D-01</td>
</tr>
</tbody>
</table>

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**Table 3**

Dipole moment for the MgF ground state at \( r_e \) from various calculations.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Dipole moment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FD-HF</td>
<td>3.1005 D</td>
<td>Kobus et al. [10]</td>
</tr>
<tr>
<td>MHF</td>
<td>3.1005 D</td>
<td>Kobus et al. [10]</td>
</tr>
<tr>
<td>SCF</td>
<td>3.098 D</td>
<td>Langhoff et al. [12]</td>
</tr>
<tr>
<td>SDCI</td>
<td>3.048 D</td>
<td>Langhoff et al. [12]</td>
</tr>
<tr>
<td>CPF</td>
<td>3.077 D</td>
<td>Langhoff et al. [12]</td>
</tr>
<tr>
<td>CASSCF</td>
<td>2.8611 D</td>
<td>Fowler &amp; Sadlej [11]</td>
</tr>
<tr>
<td>MRCI+Q</td>
<td>3.126 D</td>
<td>Wu et al. [9]</td>
</tr>
<tr>
<td>ACPF</td>
<td>3.004 D</td>
<td>This work*</td>
</tr>
</tbody>
</table>

*Optimization result, which is slightly different than the single point calculation at the experimental \( r_e \).
range of the spectroscopic data and has a maximum absolute value at larger r before returning to zero at long range (Fig. 2). For comparison, Fig. 2 includes values from an MRCI+Q calculation from the literature [9]. The ACPF dipole moment shows an abrupt change at \( r \approx 3.6 \text{ Å} \), while the MRCI+Q curve is smoother. This type of variation with \( r \) is characteristic of ionic molecules which dissociate to neutral fragments. Near equilibrium the dipole moment function is approximately linear but at large internuclear separation there is a curve crossing with at least one potential energy function in which the charge separation is small (i.e., the character of the ground state wavefunction changes rapidly from Mg\(^+\)F to MgF). Based on the electronegativity of F and the first ionization potential of Mg [29], this curve crossing occurs near 3.39 Å.

For MgF the change from ionic to covalent bonding happens outside the data range so should not affect our calculation of the line intensities. Indeed, both dipole moment functions shown in Fig. 2 give very similar intensities for the observed lines. However, when the dipole moment points from the ACPF or the MRCI+Q calculations are used directly in the LEVEL program using the built-in cubic spline interpolation, the overtone transition intensities were unphysical for \( \Delta v \geq 3 \). To solve this problem different approaches were tested, including improving the numerical accuracy of LEVEL by using quadruple precision for the variables. In the end, we found that using an analytical form to represent the dipole moment data is a simple solution.

### Table 4

Fitted Padé approximant coefficients \( M_0 \) and \( a_i \) (\( i = 1 \rightarrow 7 \)) for the MRCI+Q dipole moment.

<table>
<thead>
<tr>
<th>( M_0 )</th>
<th>( a_i ) (( i = 1 \rightarrow 7 ))</th>
<th>Values</th>
</tr>
</thead>
<tbody>
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<td>( M_0 )</td>
<td>( a_i ) (( i = 1 \rightarrow 7 ))</td>
<td></td>
</tr>
<tr>
<td>1.230 a.u.</td>
<td>( 0.814298298376826 )</td>
<td></td>
</tr>
<tr>
<td>0.31769561202887</td>
<td>( 0.490123252940770 )</td>
<td></td>
</tr>
<tr>
<td>3.12269237848287</td>
<td>( 3.950123252940770 )</td>
<td></td>
</tr>
<tr>
<td>104.976868847063</td>
<td>( 96.1926230543182 )</td>
<td></td>
</tr>
<tr>
<td>20.421738988439</td>
<td>( 12.3456789980123 )</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Padé approximant representation of the dipole moment

Following the work on hydrogen halide ground states by Li et al. [24] we take the dipole moment function in the form of a Padé approximant as:

\[
M(x) = M_0 \frac{(1+x)^3}{1+\sum_{i=1}^{7} a_i x^i}
\]

in which \( x = (r - r_e)/r_e \), \( M_0 \) is the dipole moment at \( r_e \), and \( a_i \) are the fitting coefficients. This functional form has the correct \( r^3 \) limiting behavior at small \( r \) and \( r^{-4} \) for large \( r \) [36,37]. For the literature MRCI+Q/aug-cc-pVQZ-dk dipole moment [9], the \( M_0 \) value was set to 1.23 a.u. (3.126 D), which corresponds to the experimental \( r_e \) (1.7499 Å), not the MRCI+Q calculated \( r_e \) (1.7640 Å). The corresponding \( a_i \) coefficients obtained from the least squares fit are listed in Table 4. Note the MRCI+Q \( D_e \) (\( \sim 37827 \text{ cm}^{-1} \)) and the potential curve are similar to our ACPF results. The RMS (root mean square) of the fit using all of the MRCI+Q data (1.5 Å to 4 Å) is 3.6E-3 a.u. The obtained analytical function (Eq. (4)) and the literature dipole moment points are plotted in Fig. 3. The dipole moment points from both the ACPF and the MRCI+Q calculations are provided as supplementary data files (S1 and S2). The analytic dipole moment function is smooth and has good behavior at both \( r = 0 \) and \( r \rightarrow \infty \); therefore, it is a physically acceptable function for intensity calculations for MgF. For the ACPF points, it was difficult to obtain a satisfactory simple analytical dipole moment function. Therefore, only the Padé representation of the MRCI+Q dipole moment data was used in the final list calculation with the EMO potential. The transition dipole moments (TDMs) from this Padé function are compared in Fig. 4 with the results directly obtained with the \( ab \text{ initio} \) dipole moment points of the ACPF and MRCI+Q calculations.
4. Line list

Although MgF has a $^2\Sigma^+$ ground state, the spin-rotation splitting is small and is not observed in the vibration-rotation emission spectrum [2]. MgF was therefore treated as a $^1\Sigma^+$ state [2] for the purposes of generating vibration-rotation line lists. Using the EMO potential for $^{24}$MgF and the Padé form of the MRCI+Q dipole moment [9], ro-vibrational line lists (Supplementary tables S3, S4, S5) were obtained for $^{24}$MgF, $^{25}$MgF, and $^{26}$MgF with Le Roy’s LEVEL program [18]. As expected, LEVEL produces transitions nearly identical to those from dPotFit for $^{24}$MgF. LEVEL also produces transition dipole matrix elements, the corresponding Einstein A values for each line and a set of band constants ($B, D, H, ...$) for each vibrational level (Table S6, supplementary). These band constants are useful for simulating spectra with a program such as PGOPHER [38]. Line lists for all possible allowed transitions with $v=0-8$, $N \leq 100$, with $\Delta N=\pm 1$, are calculated for the $^{24}$MgF, $^{25}$MgF, and $^{26}$MgF isotopologues and available as supplementary files (S3, S4 and S5). Born-Oppenheimer breakdown effects were ignored in the line list calculations since Mg and F are relatively heavy nuclei. For most of the observed ro-vibrational transitions of $^{24}$MgF, the differences between the calculated and the observed transitions from Barber et al. [2] are less than 0.005 cm$^{-1}$.

The calculated emission line intensities, I, for $^{24}$MgF (at 1823 K) are presented in Fig. 5 as an overview and in Fig. 6 for a short segment of the observed spectrum [2]. These intensities (in units of s$^{-1}$/molecule) are estimated as relative photon emission rates [39]:

$$I = A \left[ \frac{g_{\text{upper}} e^{-\frac{E_{\text{upper}}}{kT}}}{Q} \right],$$

(5)

in which Q is the partition function, $A$ is the Einstein A coefficient (s$^{-1}$) and $g_{\text{upper}}$ is the upper state degeneracy. As expected, the strongest spectra appear in the 600–800 cm$^{-1}$ range, corresponding to the $\Delta v=1$ transitions. For the overtone bands, the intensities for $\Delta v=3$ and, to a lesser extent, $\Delta v=4$ are anomalously low, but the overall pattern of band intensities is reasonable. Presumably the specific shape of the dipole moment function of MgF is responsible for the deviations from the typical decrease in intensity of about a factor of 10 for each increase in $\Delta v$ [40].

As a test of our line lists we simulated the emission spectrum of $^{24}$MgF using PGOPHER for comparison with the observed spectrum of Barber et al. [2] recorded with a sample temperature of 1823 K. The positions and relative intensities agree well as presented in Fig. 6.

5. Discussion of overtone intensities

In our initial work, we calculated the line intensities using the ACPF/cc-pv5z dipole moment points directly in LEVEL with cubic spline interpolation. We noted that line intensities of $\Delta v=3$ overtone bands were weak and the intensities increased slightly with $\Delta v$ for $\Delta v=4-7$ (Fig. 4). This increase is unphysical. We then tried the dipole moment points from an MRCI+Q/aug-cc-pVQZ-dk calculation [9], and some improvement was noted (Fig. 4). LEVEL was also converted from using Double Precision variables to Quadruple Precision, but there was little effect except for very high $\Delta v$ values outside the range of interest. Finally, by fitting the MRCI+Q dipole moment points with an analytical function, Eq. (4), a more reasonable intensity distribution was obtained (Fig. 4). Very recently a similar effect and a similar solution using analytical dipole moment functions was described by Medvedev et al. [40] for CO overtone.

The intensity of a line as measured by the Einstein A value is given by the expression [19,39]:

$$A = 3 \times 10^{-5} \frac{S(f,J')}{2J+1} \left[ |\Psi_{v,J}(r)|^2 |\Psi_{v',J'}(r)|^2 \right]^2,$$

(6)

in which $A$ is in s$^{-1}$ units, $M(r)$ is the dipole moment function in debye, $v$ the transition frequency in cm$^{-1}$, $S(f,J')$ is a Hönl-London rotational factor, and $\Psi_{v,J}$ and $\Psi_{v',J'}$ are the vibrational wave functions which depend on $J$ from the centrifugal potential. From Eq. (6), the two main factors that influence the transition intensities between two states in a given electronic state are the wave function $\Psi_{v,J}$ and the dipole moment function $M(r)$. The vibrational wave function $\Psi_{v,J}$ and the transition frequencies $v$ are determined by the effective molecular potential function $V_{\text{eff}}(r)=V+V_{\text{cent}}$ [39], which in this work uses an accurate fitted EMO potential function for $V$. In our case, the main factor that influences the calculated intensities is therefore the dipole moment function $M(r)$. For fundamental transitions, both the present ACPF and the literature [9] MRCI+Q points produce similar relative intensities compared to the observed spectrum [2] of $^{24}$MgF. For overtone transitions, however, there can be numerical problems associated with interpolation of discrete points that contain small amounts of “noise” (i.e., ab initio points are not in fact “smooth”, for example, because of the convergence criteria used). Using an analytical form to represent the ab initio dipole data is a simple solution [40]. The Padé approximant [24,36,37], Eq. (4), used in this work not only fits all the high quality MRCI+Q ab initio dipole points well, but also extrapolates properly to $R=0$ and $R=\infty$.  

![Fig. 4. Distribution of the TDMs calculated using different dipole moment functions. Notice that the $\Delta v=3$ (near 2000 cm$^{-1}$) TDMs are anomalously weak and there is a strong rotational dependence.](image)

![Fig. 5. Calculated overall emission intensity distribution for $^{24}$MgF transitions in the range of $v \leq 8$, $N \leq 100$, $\Delta v=0-8$, and $\Delta N=\pm 1$, at 1823 K. Dipole moment function uses the fitted Padé approximant Eq.(4) with the MRCI+Q data from Ref. [9].](image)
6. Conclusion

Line lists are calculated for the ground state MgF isotopologues with an accurate empirical potential function which reproduces the observed transitions within experimental uncertainty. The intensities of the transitions are predicted with high level \textit{ab initio} ACPF/cc-pv5z and MRCI + Q/aug-cc-pvqz-dk dipole moment data. For overtone transitions, an analytical representation of the \textit{ab initio} dipole moment function gives a more reliable estimate of line intensities. In particular, a Padé approximant based on the MRCI + Q/aug-cc-pvqz-dk dipole moment points is used to calculate the line intensities. All transitions for $v < 9$, $\Delta v = 0-8$, $\Delta N = \pm 1$, $N \leq 100$ were predicted for $^{25}$MgF, $^{24}$MgF, and $^{23}$MgF.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2017.03.019.

References


Fig. 6. Comparison of the observed and calculated MgF emission spectrum for part of the R-branch at 1823 K. Experimental spectrum (solid; black) is from Barber et al. [2]. Simulated line profiles (blue dotted line) were obtained with PGOPHER [37].


