Spectroscopic characterization of the $F^1\Pi_1$ 'Rydberg' state of the MgO molecule

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Abstract

The $F^1\Pi_1$ 'Rydberg' state of $^{24}Mg^{16}O$ has been characterized by two-color Resonance-Enhanced Two-Photon Ionization (R2PI) spectroscopy in the 37 000–39 000 cm^{-1} region. Several rotationally resolved bands, assigned to $^{24}Mg^{16}O(F^1\Pi_1 \leftarrow X^1\Sigma^+)$ vibronic transitions, have been analyzed to yield spectroscopic constants for the $F^1\Pi_1$ state. Consistent with the ab initio calculations of Peyerimhoff and co-workers, the $F^1\Pi_1$ state appears to have mixed Rydberg–valence character.
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1. Introduction

We are currently spectroscopically characterizing 'Rydberg' type states of diatomic metal oxide molecules, in preparation for single-collision reactive studies of these neutral, but 'almost-ion' species with H_2 and CH_4. The ground-state and the low-lying excited states of the MgO molecule have been well-characterized by optical spectroscopy and laser–magnetic-resonance studies [1–7]. Theoretical studies [8–11] have also been carried out on both the ground state and excited states of MgO up to ~50 000 cm^{-1} in energy. The $X^1\Sigma^+$ ground-state, although formally $Mg^{+2}O^{-2}$ in

character, in fact appears to have a substantial amount of Mg^+O^- 'open-shell' character [8–11]. There are also very low-lying $A^1\Pi_1$ and $a^3\Pi$ states (~3000 cm^{-1}) which are formally Mg^+O^- in character. At much higher energies (36 000–40 000 cm^{-1}), there are $^1\Pi_1$ and $^3\Pi$ states which are formally 'Rydberg' in character, e.g., MgO^+ surrounded by a diffuse electron cloud. However, Peyerimhoff and co-workers [11] have found that at least for the lower-lying of such states (and the analogous $^1\Sigma^+$ states), there is 'mixed' valence–Rydberg character. Singh [7] has experimentally recorded a single band at 37 879 cm^{-1} to what is apparently the lowest of these $^1\Pi_1$ 'Rydberg' states, which he has tentatively assigned as the $(F^1\Pi_1 \leftarrow X^1\Sigma^+)MgO$ (0,0) transition.

We have observed a plethora [12] of vibronic transitions in the 36 000 to 40 000 cm^{-1} spectral

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region. They consist mainly of three types, when rotationally resolved: simple $(\Omega' = 0) \leftarrow (\Omega'' = 0)$ transitions with no Q-branch; $(\Omega' = 1) \leftarrow (\Omega'' = 0)$ transitions, with typical P, Q, R structure, and $(\Omega' = 2) \leftarrow (\Omega'' = 2)$ transitions (P, Q, R structure, but with R(0), R(1), P(2), Q(1) lines missing). The first two sets of transitions have been shown [12] to originate from several of the well-characterized vibrational levels of the $MgO(X^1\Sigma^+)$ ground-state [1–3], and the third set [12] from vibrational levels of the lowest-lying metastable triplet state, $MgO(a^3\Pi_2)$ [4–6]. Many of the spectra are beautifully well-resolved, and are almost 'text-book' examples of these kinds of transitions. The spectra reported here are of the $(\Omega' = 1) \leftarrow (\Omega'' = 0)$ type, and have been shown to be due to the $F^1\Pi_1 \leftarrow X^1\Sigma^+$ electronic transition of the $^{24}Mg^{16}O$ molecule. Several rotationally resolved bands are consistently assigned to the $F \leftarrow X$ transition, and we confirm Singh's (0,0) band assignment [7]. The vibrational and rotational constants we have determined for the $F^1\Pi_1$ state are also qualitatively consistent with Peyerminhoff and co-workers [11] notion that this state has 'mixed' valence–Rydberg character.

2. Experimental

The experimental apparatus has been described in detail elsewhere [12,13]. Briefly, 532 nm radiation from a Molectron MY-32/10 Q-switched Nd:YAG laser is focused onto the surface of a rotating pure Mg rod which is inside a 100 l vacuum chamber (operating pressure $\sim 5 \times 10^{-5}$ Torr) and is *slightly beyond* the 2-mm exit hole of a gas source. The laser-vaporization products are entrained in a gas pulse produced by a general valve backed by 40–100 psi of helium or neon gas containing 1% N_2O. Mg species from the discharge react with the N_2O in the gas pulse to form MgO, and the ensuing supersonic expansion cools the MgO molecules to rotational temperatures of ~ 5–15 K, depending on the expansion conditions. The beam traverses a 60 cm region through a skimmer before entering the ionization region of a one meter time-of-flight mass spectrometer. Here the MgO molecules are interrogated with the outputs of two simultaneously pumped dye lasers,

which act in concert to ionize the neutral species. Resonance-Enhanced Two-Photon Ionization (R2PI) spectra are obtained by frequency scanning the output of one of the two dye lasers while holding the other dye laser constant in frequency, monitoring the MgO^+ signal in the mass spectrum. The ultraviolet radiation used for the resonant step in the two-photon ionization process was obtained by non-linear frequency doubling (KDP or BBO crystals) of a dye laser output. Some single-dye-laser spectra were also taken where 355 nm radiation from the YAG laser which pumped the dye laser was used for the ionization step.

3. Results and discussion

We have recorded five vibrational bands of the $F \leftarrow X$ transition of $^{24}Mg^{16}O$ with sufficient signal-to-noise for accurate rotational analysis. Shown in Fig. 1 is the (1,1) band (of $^{25}Mg^{16}O$ to illustrate the excellent signal-to-noise of the spectra (^{25}Mg has only 10% abundance!)). Because the B constants of the $X^1\Sigma^+$ and $F^1\Pi_1$ states are so similar, $\Delta v = 0$ transitions are very strong, due to the Franck–Condon principle, and $\Delta v \neq 0$ transitions are very weak, unlike the $MgO(E^1\Sigma^+ \leftarrow X^1\Sigma)$ electronic transitions [12] or electronic transitions [12] from the $MgO(a^3\Pi_2)$ state.

Shown in Table 1 are the transition wavenumbers and B'', B' rotational constants of $^{24}Mg^{16}O$ resulting from our rotational analyses. Our transition wavenumbers for the band origins of the
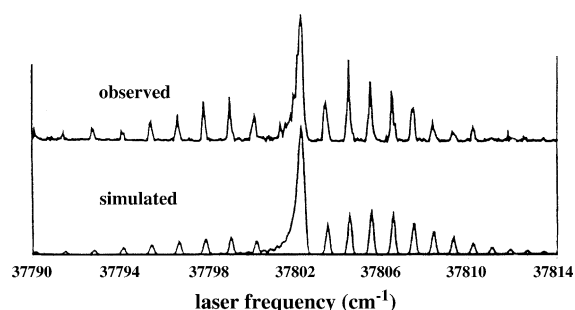

Fig. 1. High-resolution spectrum (top) of the F–X (1,1) band of the minor isotope $^{25}Mg^{16}O$; computer simulation (bottom): $T = 10$ K; $B'' = 0.550$ cm^{-1}; $B' = 0.538$ cm^{-1}.

(0,0) and (1,1) bands are consistent with those estimated earlier by Singh [7], as is our B'_o value. Our B''_v values are also consistent with the very accurate B''_v values quoted in a laser–magnetic-resonance study [1] of MgO($X^1\Sigma^+$). The final electronic, rotational, and vibrational spectroscopic constants for the $F^1\Pi_1$ state determined from the data in Table 1 are shown in Table 2.

Our (v', v'') assignments have been confirmed by isotopic splitting measurements (see Table 3). The MgO molecule has two naturally occurring minor isotopes, $^{25}Mg^{16}O$ and $^{26}Mg^{16}O$ (~10% and ~11% abundance each). From the vibrational constants for the $F^1\Pi_1$ state in Table 2, and the accurate vibrational constants [1] known for the $X^1\Sigma^+$ state, the band origins for the $^{25}Mg^{16}O$ and $^{26}Mg^{16}O$ isotopomers can be predicted. The isotopic shifts observed are very consistent with the predicted values.

In Table 4, the $F^1\Pi_1$ spectroscopic constants are compared with those for other states of MgO and MgO$^+$. Peyerimhoff and co-workers [11] have examined the molecular orbital occupations of many excited states of the MgO molecule. The $F^1\Pi_1$ state, near its R_e value, has a substantial amount of Rydberg character, and formally correlates with the MgO$^+$($A^2\Sigma^+$) first excited ionic state and the diffuse $3p\pi$ Rydberg electron surrounding the ionic state [11]. However, one would expect a 'true' Rydberg state to have R_e and ω_e values similar to that of the 'core' MgO$^+$($A^2\Sigma^+$) ionic state, calculated by Bauschlicher and co-workers [10], to be 1.70 Å and 902 cm^{-1}, respectively. The values for the $F^1\Pi_1$ state, 1.77 Å and

705 cm^{-1}, are in fact between those of MgO$^+$($A^2\Sigma^+$) and those of the valence, ionic (Mg$^+$O$^-$) $A^1\Pi_1$ state, where $R_e = 1.86$ Å, and $\omega_e = 664.5$ cm^{-1}. This is consistent with Peyerimhoff's analysis [11], indicating that the lowest 'Rydberg' states are in fact mixed 'Rydberg/ionic-valence' states. There are also complications caused by multiple avoided crossings between repulsive valence $^1\Pi_1$ states and these 'Rydberg' states (see Fig. 7 in [11]), leading to 'multiple-well' adiabatic $^1\Pi_1$ potential curves in this energy region. This could also cause a lowering of the ω_e value for the $F^1\Pi_1$ state. True Rydberg states must

Table 2
Derived spectroscopic constants for $^{24}Mg^{16}O(F^1\Pi_1)$ from this work (cm^{-1} unless indicated)

T_e	ω_e	$\omega_e x_e$	B_e	α_e	R_e (Å)
37 919 ($\pm$2)	705 ($\pm$2)	4.5 ($\pm$0.2)	0.563 ($\pm$0.002)	0.0055 ($\pm$0.0005)	1.766 ($\pm$0.003)

Table 3
Isotopic splittings for $F \leftarrow X$ bands (see text)

Band	Calculated[a]		Observed	
	40/41	40/42	40/41	40/42
(0,0)	−0.3	−0.6	−0.3	−0.5
(1,1)	−1.0	−1.8	−1.0	−1.7
(2,2)	−1.6	−3.0	–	−3.1
(1,2)	−6.9	−13.4	−7.0	−13.5
(1,0)	+5.2	+10.0	+5.3	+10.0

[a] $\omega''_e = 785.218$, $\omega_e x''_e = 5.1327$, $\omega_e y''_e = 0.01649$ [1], $\omega'_e = 705$, $\omega_e x'_e = 4.5$ (this work).

Table 1
$^{24}Mg^{16}O(F^1\Pi_1 \leftarrow X^1\Sigma^+)$ bands observed and rotationally analyzed (cm^{-1})

Band	Band origins		$B''(\pm 0.002)$	$B'(\pm 0.002)$
	Observed	Predicted[a]		
(0,0)	37 879.2(37 879)[c]	37 879.1	0.572(0.5721)[b]	0.557(0.559)[c]
(1,1)	37 802.3(37 801)[c]	37 800.1	0.567(0.5668)[b]	0.551
(2,2)	37 719.1	37 722.2	0.560(0.5615)[b]	0.545
(1,2)	37 036.7	37 035.2	0.562(0.5615)[b]	0.551
(1,0)	38 574.6	38 575.1	0.574(0.5721)[b]	0.552

[a] $\omega''_e = 785.218$, $\omega_e x''_e = 5.1327$, $\omega_e y''_e = 0.01649$ [1], $\omega'_e = 705$, $\omega_e x'_e = 4.5$ (see Table 2).
[b] Ref. [1].
[c] ('Q-heads') [7].

Table 4
Spectroscopic constants for selected $^{24}Mg^{16}O$ (singlet) and $^{24}Mg^{16}O^+$ (doublet) electronic states

Species	Electronic state	T_e (cm^{-1})	ω_e (cm^{-1})	B_e (cm^{-1})	R_e (Å)
MgO$^+$	A$^2\Sigma^{+}$[a]	6760	902	0.608	1.70
MgO$^+$	X$^2\Pi$ [a]	0	745	0.536	1.81
MgO	F$^1\Pi_1$[b]	37 919	705	0.563	1.76$_6$
MgO	E$^1\Sigma^{+}$[c]	37 717	718	0.532	1.81$_7$
MgO	A$^1\Pi_1$[d]	3558.6	664.5	0.5054	1.8643
MgO	X$^1\Sigma^{+}$[d]	0	785.2	0.5748	1.7482

[a] Ref. [10].
[b] This work.
[c] Ref. [12].
[d] Ref. [1].

be even higher in energy, and we plan to search for and characterize them by R2PI spectroscopy.

References

[1] P. Murtz, H. Thummel, C. Pfelzer, W. Urban, Mol. Phys. 86 (1995) 513.
[2] T. Torring, J. Hoeft, Chem. Phys. Lett. 126 (1986) 477.
[3] Y. Azuma, T.R. Dyke, G.K. Gerke, T.C. Steimle, J. Mol. Spectrosc. 108 (1984) 137.
[4] P.C.F. Ip, K.J. Cross, R.W. Field, J. Rostas, B. Bourguigunon, J. McCombie, J. Mol. Spectrosc. 146 (1991) 409.
[5] B. Bourguigunon, J. Rostas, J. Mol. Spectrosc. 146 (1991) 437.
[6] K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules., Van Nostrand, New York, 1979.
[7] M. Singh, J. Phys. B 6 (1973) 1339.
[8] S.R. Langhoff, C.W. Bauschlicher Jr., H. Partridge, J. Chem. Phys. 84 (1986) 4474.
[9] C.W. Bauschlicher Jr., H. Partridge, Chem. Phys. Lett. 205 (1993) 479.
[10] H. Partridge, S.R. Langhoff, C.W. Bauschlicher Jr., J. Chem. Phys. 84 (1986) 4489.
[11] H. Thummel, R. Kotz, S.D. Peyerimhoff, Chem. Phys. 129 (1989) 417.
[12] D. Bellert, Katherine L. Burns, Nguyen-Thi Van-Oanh, Jinjin Wang, W.H. Breckenridge (submitted).
[13] D. Bellert, K.L. Burns, R. Wampler, W.H. Breckenridge, Chem. Phys. Lett. 322 (2000) 41.