

Laser Spectroscopic Studies of the E 1£+ State of the MgO Molecule

J.J. Wang, N.-T. Van-Oanh, D. Bellert, W.H. Breckenridge, M.-A. Gaveau, Eric Gloaguen, B. Soep, J.-M. Mestdagh

▶ **To cite this version:**

J.J. Wang, N.-T. Van-Oanh, D. Bellert, W.H. Breckenridge, M.-A. Gaveau, et al.. Laser Spectroscopic Studies of the E 1£+ State of the MgO Molecule. Chemical Physics Letters, 2004, 392, pp.62-67. 10.1016/j.cplett.2004.04.083 . hal-00085000

HAL Id: hal-00085000
https://hal.science/hal-00085000

Submitted on 28 Jul 2006

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Laser Spectroscopic Studies of the E $^1\Sigma^+$ State of the MgO Molecule

Jinjin Wang, Nguyen-Thi Van-Oanh, D. Bellert, W. H. Breckenridge*
Department of Chemistry
University of Utah
315 So. 1400 East, Rm. 2020
Salt Lake City, UT 84112-0850
USA

Marc-Andre Gaveau, Eric Gloaguen, Benoit Soep, J.-M. Mestdagh
C.E.A. SACLAY
DSM/DRECAM/SPAM
Bâtiment 462
91191 - Gif sur Yvette Cedex
FRANCE

*Corresponding author:
e-mail: breck@chem.utah.edu
Fax: 801-587-9919
Phone: 801-581-8024

Abstract

The E $^1\Sigma^+$ state of $^{24}Mg^{16}O$ has been characterized by two-color Resonance-Enhanced Two-Photon Ionization (R2PI) spectroscopy in the 36,000 – 40,000 cm^{-1} region. Several rotationally resolved bands, assigned consistently to $^{24}Mg^{16}O$(E $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$) vibronic transitions, have been analyzed. The effective $B_{v'}$ ($v' = 0 – 8$) constants determined exhibit an unusual variation with v'. Possible causes of this variation are discussed. The vibrational level spacings in the E $^1\Sigma^+$ state ($v' = 0 – 7$) also provide evidence for a weak homogeneous ($\Omega = 0^+$) perturbation. Estimated spectroscopic constants for the E $^1\Sigma^+$ state are reported.

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 fact appears to have a substantial amount of Mg^+O^- "open-shell" character [8-11]. At much higher energies (36,000 – 40,000 cm^{-1}), there are $^1\Sigma^+$ and $^1\Pi_1$ states which are formally "Rydberg" in character, e.g., MgO^+ states surrounded by diffuse electron clouds. However, Peyerimhoff [11] has found that at least for the lower-lying of these states there is "mixed" valence/Rydberg character. Singh [7] has experimentally recorded and rotationally resolved a single band at 37,683.5 cm^{-1} to what is apparently the lowest of these "Rydberg" states, which he tentatively assigned to the (E $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$)MgO (0,0) transition. Antić-Jovanović, *et al.* [12], confirmed the E-X(0,0) assignment of Singh by means of $^{24}Mg^{16}O/^{24}Mg^{18}O$ isotopic splittings in the (E $^1\Sigma^+$ - A $^1\Pi_1$) transitions.

We have observed a plethora [13,14] of vibronic transitions of MgO in the 36,000 cm^{-1} to 40,000 cm^{-1} spectral 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 [13] to originate from several of the well-characterized vibrational levels of the MgO(X $^1\Sigma^+$) ground-state [1-3], and the third set [14] 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 "text-book" examples of these kinds of transitions. The spectra described here are of the simplest $(\Omega' = 0) \leftarrow (\Omega'' = 0)$ type, and have been shown to be due to the E $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$ electronic transition of the $^{24}Mg^{16}O$ molecule. Several rotationally-resolved vibronic bands have been consistently assigned to E $\leftarrow$ X vibronic transitions. Vibrational spectroscopic constants ω_e' and $\omega_e x_e'$ for the E $^1\Sigma^+$ state have been determined from this data. However, the rotational constants $B_{v'}$ show very unusual variations with v′, and the possible causes of these variations are discussed.

Experimental

The experimental apparatus has been described in detail elsewhere [13-15]. 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 liter vacuum chamber [operating pressure ~5 × 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. R2PI (Resonance Two-Photon Ionization) 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 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.

Results and Discussion

Shown in Fig. 1 is a typical high-resolution Σ-Σ spectrum, the E-X(0,0) band, along with a computer spectral simulation. Shown in Table 1 are the results of rotational analyses of several such bands, and their consistent assignments to E-X(v′,v″) transitions. Isotopic splittings were consistent with the E-X(v′,v″) assignments. For example, the measured isotopic splittings for the mass 41 and 42 isotopes for the E-X(1,0) transition were –5.3 cm^{-1} and –10.5 cm^{-1}, respectively, while the calculated values from the vibrational constants of the E $^1\Sigma^+$ and X $^1\Sigma^+$ states were –5.3 and –10.3 cm^{-1}, respectively. Note that the $B_{v''}$ constants are known from earlier high resolution studies [1], and our $B_{v''}$ values are consistent with these values (within our ± 0.002 cm^{-1} estimated experimental error).

It is seen immediately in Table 1 that there is a sudden, dramatic drop in $B_{v'}$ values between v′ = 1 and v′ = 2, and that the $B_{v'}$ values for v′ = 3 to 8 are approximately constant, decreasing slightly at high v′. This is often a signature [16,17] (but see below) of a heterogeneous "Λ-doubling" gyroscopic (rotationally-dependent) perturbation by a *higher-lying* state with Ω = 1. Thus the B'_v values of the E $^1\Sigma^+$ state (all levels have "e" symmetry) are "pushed down" by the rotationally-dependent perturbation, while the B'_v values for one component (e) of the Ω = 1 state would be "pushed up." We will discuss this further after we examine the data for the E $^1\Sigma^+$(v′; J′ = 0) vibrational energies.

Shown in Table 2 are the energies , $\Delta G_{v'+1/2}$ values and $\Delta^2 G_{v'}$ (2^{nd} difference) values of the E($^1\Sigma^+$, v′ = 0 – 7) vibrational levels, calculated from the band-origins in Table 1, and the following consistent energies from this (and other) [18] work for v″ = 1 to v″ = 4: 775.0, 1539.9, 2293.1, and 3036.1 cm^{-1}, respectively. (These energies can be characterized fairly accurately with values of ω''_e = 785.7 ± 0.5 cm^{-1} and $\omega_e x''_e$ = 5.33 ± 0.30 cm^{-1}.) In Figure 2 is shown a Birge-Sponer plot of $\Delta G_{v'+1/2}$ versus v′ + 1 for the E $^1\Sigma^+$ state. From the slope and intercept of this plot, ω'_e = 714.1 ± 0.9 cm^{-1} and $\omega_e x'_e$ = 4.14 ± 0.09 cm^{-1} **[new values to be provided by Marc-Andre]** for the E($^1\Sigma^+$) state of $^{24}Mg^{16}O$. There appear to be small oscillations of $\Delta G_{v'+1/2}$ values about the "best-fit" Birge-Sponer straight line which are outside our estimated experimental errors, possibly indicating homogeneous ($\Omega = 0^+/\Omega = 0^+$) vibrational perturbations [17]. This is much more obvious from the $\Delta^2 G_{v'}$ (2^{nd} difference values) in Table 2, which are plotted versus v′ in Fig. 3. But the general trends in the $\Delta G_{v'+1/2}$ values are consistent with a simple "Morse-function" type shape for the E $^1\Sigma^+$ potential curve for v′ ≤ 7.

We now return to our discussion of the unusual variation with v′ of the $B_{v'}$ values in Table 1. The most common "Λ-doubling" interaction for a $^1\Sigma^+$ state is with a nearby bound $^1\Pi_1$ state [16,17]. There are two known $^1\Pi_1$ states nearby, the F $^1\Pi_1$ and G $^1\Pi_1$ states [13,18]. Their potential minima are indeed higher in energy than that of the E $^1\Sigma^+$ state: 37,919 cm^{-1} and 39,181 cm^{-1}, respectively, versus 37,718 cm^{-1} for the E $^1\Sigma^+$ state (see Table 4). However, strong Λ-doubling interactions with the E $^1\Sigma^+$ state can probably be ruled out experimentally for these two states. The $^1\Sigma^+$ rotational states all have "e" parity, and they can only couple with the "e" levels of the $^1\Pi_1$ rotational states. Since the Q-branches of $^1\Pi_1 \leftarrow X\ ^1\Sigma^+$ transitions only go to "f" levels and P,R branches only go to "e" levels [16,17], any strong Λ-doubling can be detected by

looking for "combination defects" [16] in Q-branch versus P,R branch transitions as J′ increases (the Λ-doubling splitting between the J′ "e" and "f" levels due to the interaction with $^1\Sigma^+$ "e" levels is proportional to J(J + 1).) [16,17] A value of "q" can be derived, which is the difference between the "effective" B values for the "e" and "f" levels. For very high J′ values in earlier data [19,20] for the F-X(0,0) and the G-X(1,0) bands (from isotopic splittings, we have shown [18] that the band tentatively assigned by Singh [20] to the G-X(0,0) band is probably the G-X(1,0) band), the combination defects were shown to be very small ($q \leq 0.0001$ cm^{-1}), thus making it unlikely that the F $^1\Pi_1$ and G $^1\Pi_1$ states are the causes of the unusual E($^1\Sigma^+$) state perturbations observed here, where the sudden drop of B'_v values from v′ = 1 to v′ = 2 requires much larger (and quite unusual) "effective" q-values on the order of ~0.01 cm^{-1}.

We thus examine other possible causes of the $B_{v'}$ variation. One possibility is that the repulsive wall of *another*, lower-lying $^1\Pi_1$ state potential curve crosses the inner limb of the E $^1\Sigma^+$ potential curve just above the E $^1\Sigma^+$(v′ = 2) eigenstate energy. Rotationally induced coupling between the repulsive Ω = 1(e) levels and the Ω = 0^+(e) levels should be approximately proportional [16,17] to the inverse of the energy difference, ΔE, between the two potential curves at the E $^1\Sigma^+$(v′) inner turning points, for v′ = 2 or higher. This difference ΔE should increase from v′ = 2 to v′ = 8 if the $^1\Pi_1$ curve is slightly more repulsive than the inner limb of the E $^1\Sigma^+$ potential curve.

To provide "plausibility" evidence for this sort of tentative postulate, we assume that the B'_o = 0.524 cm^{-1} value is essentially unaffected by the higher-lying repulsive curve-crossing (this may not be *quantitatively* true, of course, as it could be slightly "pushed-up" in value), and we further assume that α'_e, the parameter describing the "normal" decreases in B'_v values with v′,

can be estimated rather well using the Pekeris relationship [16] for a Morse curve (since the Birge-Sponer plot in Fig. 1 indicates reasonable "Morse" type behavior, over-all):

$$B_v = B_e - \alpha_e(v + ½) \quad (1)$$

$$\alpha_e \text{ (Morse curve)} = \frac{6\left[(\omega_e x_e)(B_e)^3\right]^{½}}{\omega_e} - \frac{6(B_e)^2}{\omega_e} \quad (2)$$

Shown in Table 3 are the B'_v(exptl.) values determined from the data in Table 1, as well as the B'_v(predicted) values assuming $B'_o = 0.524$ and $\alpha'_e = 0.0042$ (from the Pekeris relationship, equation (2)). Also shown is the difference, q = B'_v(exptl.) – B'_v(predicted), which is the estimated "Λ-doubling" coupling parameter (given our assumption that B'_o is a "true" value). It can be seen that the estimated "q" values are consistent with our postulate, in that the absolute value of q falls from ~0.018 cm^{-1} at v′ = 2 to essentially zero at v′ = 8. Thus, this postulated mechanism is certainly *feasible*. On the other hand, it is not obvious from the *ab initio* calculations [11] what the repulsive $^1\Pi_1$ state could be, and why it wouldn't also undergo obvious avoided crossings with the bound-state F $^1\Pi_1$ and G $^1\Pi_1$ potential curves in this energy region.

It is also possible that the cause of the perturbation is due to "Ω-doubling" caused by similarly repulsive $^3\Sigma_1^-$, $^3\Sigma_1^+$, $^3\Pi_1$, or $^3\Delta_1$ triplet states (all have "Ω = 1" levels, although the $^3\Sigma$ states are formally "case b," where Ω is not really a good quantum number). The *ab initio* calculations of Peyeriminhoff and co-workers do show curve crossings of the repulsive limbs of both a lower-lying $^3\Pi$ state and a lower-lying $^3\Sigma^-$ state near the bottom of the E $^1\Sigma^+$ potential well, (See Fig. 8 in Ref. [11].)

These $^3\Sigma_1^-$ or $^3\Pi_1$ repulsive curves will also have $\Omega = 0^+$ components (unlike $^1\Pi$, $^3\Delta$, $^3\Sigma^+$, or $^1\Sigma^-$ states) [11,17], which could result [Ref. 17, p. 343] in spin-orbit-induced homogeneous ($\Delta\Omega = 0$) couplings with the E $^1\Sigma^+$ state. The oscillations in the Birge-Sponer plot in Fig. 2 (see Fig. 3) may be due to such couplings. Also, we had great difficulty in recording any E-X(3,v″) bands, and were finally able (using slow scans and the averaging of many spectra) to identify and make a rough rotational analysis of the E-X(3,0) band. This could be due to weak singlet-to-triplet predissociation (no rotational line-broadening) of the E $^1\Sigma^+$(v′ = 3) vibrational state, which would lie just above the postulated "inner-wall" curve-crossing between the v′ = 2 and v′ = 3 vibrational levels.

The real problem with any "$^3\Sigma_1$, $^3\Pi_1$"perturbation explanation of the $B_{v'}$ variations, however, is that in pure Hund's case "a" or "b" there should be essentially *no* L-uncoupling "Λ-doubling" interaction between these states and the E $^1\Sigma^+$ state, since ΔS must be zero [16,17], so that the interaction has to be spin-orbit-induced [16] (i.e., the Ω = 1 curves must approach Hund's case "c" to interact strongly with the $\Omega = 0^+$ levels "gyroscopically"). However, the spin-orbit coupling is not that large for the 0^{-1} ion (121 cm^{-1}) [17], so that the potential curves would have to be extremely close in energy on the inner limbs to generate the large q values shown in Table 3.

Finally, we consider a very unusual explanation for this unusual $B_{v'}$ variation. The *ab initio* calculations [11] indicate that the "E $^1\Sigma^+$ state," because of avoided crossings with other repulsive valence state diabatic repulsive curves and other attractive Rydberg state diabatic potential curves at larger internuclear distances R, actually has an *adiabatic* potential curve which is of "triple-well" character, with secondary minima at R ≈ 2.7 Å and R ≈ 4.5 Å in addition to the absolute minimum at 1.8 Å. If the v′ = 0 level of the nearest "secondary

minimum" (which we shall call the H $^1\Sigma^+$ state) is close to the E $^1\Sigma^+(v' = 2)$ level, but the bound portions of the E and H state potential curves are separated by a wide potential maximum (as shown by the *ab initio* calculations [11]), then it is possible that there is a small, but significant, admixture of the H-state into the E-state wavefunctions, for $v' = 2$ or greater. This admixture could decrease with v' if the resonance-energy ΔE (which could be positive *or* negative) between vibrational eigenstate energies decreases with v' (slightly different ω'_e and/or $\omega_e x'_e$ values for the E and H states). Even very small admixtures ($\leq 6\%$) could cause the observed changes in the $B_{v'}$ values for the E-state, since the "long-range" H-state will have much smaller $B_{v'}$ values, on the order of only ~0.2 cm^{-1}. On the other hand, such small admixtures might cause only small perturbations to the E $^1\Sigma^+(v')$ *vibrational* energies (as observed) if the ω'_e values for the E and H states are similar (which is likely). This is a very speculative idea, but *ab initio* or "model" theoretical studies could confirm or deny its feasibility. We currently favor this explanation. [The "H $^1\Sigma^+$" (secondary minimum) state, of course, is not Franck-Condon accessible from the X $^1\Sigma^+(v' = 0\text{-}5)$ vibrational levels, and will be difficult to characterize experimentally.]

Our final estimates of the spectroscopic constants for $^{24}Mg^{16}O$ (E $^1\Sigma^+$) are shown in Table 5.

Acknowledgments

We gratefully acknowledge the financial support of the National Science Foundation (USA), the Petroleum Research Fund (USA), and the C.N.R.S. (France) for this research. A joint NSF-CNRS International Research Travel Grant made the collaborative aspects of this research possible. One of us (W.H.B.) would like to acknowledge useful conversations with his colleague Professor Michael Morse on the possible "double-well" mechanism for the $B_{v'}$ variations.

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

Band	Band Origin Wavenumber ($\pm$ 0.5 cm^{-1})	B'_v ($\pm$0.003)	B''_v ($\pm$0.002)
(0,0)	37 683.6 (37 683.5)[a]	0.524 (0.525)[a]	0.572 (0.572)[b]
(1,0)	38 388.5 (38 388.5)[a]	0.520	0.572 (0.572)[b]
(2,0)	39 085.8	0.498	0.572 (0.572)[b]
(3,0)	39 776.9[c]	0.499 $\pm$ 0.007[c]	0.570 $\pm$ 0.005[c] (0.572)[b]
(4,1)	39 682.0	0.498	0.567 (0.567)[b]
(4,2)	38 917.1	0.498	0.559 (0.561)[b]
(5,2)	39 590.7	0.498	0.561 (0.561)[b]
(5,3)	38 837.5	0.497	0.554 (0.556)[b]
(6,3)	39 500.8	0.496	0.555 (0.556)[b]
(7,3)	40 156.2	0.491	0.555 (0.556)[b]
(7,4)	39 413.2	0.494	0.551 (0.551)[b]
(8,5)	39 328.7	0.489	0.544 (0.545)[b]

[a] Ref. [7].

[b] Ref. [1].

[c] Low signal-to-noise.

Table 2. Energy levels of the vibrational states v′ of the E $^1\Sigma^+$ state, relative to the X $^1\Sigma^+$(v″ = 0, J″ = 0) state, calculated from the band origins in Table I (see text). Also shown are the $\Delta G_{v'+1/2}$ and $\Delta^2 G_{v'}$ (second difference) values.

v′	$E_{v'}$ (cm^{-1}) (±0.3 cm^{-1})	$\Delta G_{v'+1/2}$ (cm^{-1})	$\Delta^2 G_{v'}$ (cm^{-1})
0	37 683.6		
		704.9	
1	38 388.5		7.6
		697.3	
2	39 085.8		6.2
		691.1	
3	39 776.9		11.0
		680.1	
4	40 457.0		6.7
		673.6	
5	41 130.6		10.3
		663.3	
6	41 793.9		7.9
		655.4	
7	42 449.3		

Table 3. Rotational constants B_v of the $E\ ^1\Sigma^+$ state. (cm^{-1})

v	B_v (exptl.)	B_v (predicted)[a]	q[b]
0	0.524 (0.525)[c]	0.524	0.00
1	0.520	0.520	0.00
2	0.498	0.516	–0.018
3	(0.499)[d]	0.511	(–0.012)[d]
4	0.498	0.507	–0.009
5	0.498	0.503	–0.005
6	0.496	0.499	–0.003
7	0.493	0.495	–0.002
8	0.489	0.490	–0.001

[a] Assuming $B_o = 0.524\ cm^{-1}$ and using the Pekeris relationship (eq. 2) for a Morse curve, with $\omega_e = 714.1\ cm^{-1}$ and $\omega_e x_e = 4.14\ cm^{-1}$, to calculate $\alpha_e = 4.2\times10^{-3}$. **May change slightly**

[b] B_v(exptl.) – B_v(predicted) = q (see text)

[c] Ref. [7].

[d] From low signal-to-noise data.

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]	6 760	902	0.608	1.70
MgO^+	$X\ ^2\Pi$ [a]	0	745	0.536	1.81
MgO	$G\ ^1\Pi_1$ [b]	(39 181)[g]	(730)[g]	(0.533)[g]	(1.81)[g]
MgO	$F\ ^1\Pi_1$ [c]	37 917	709	0.560	1.77
MgO	$E\ ^1\Sigma^+$ [d]	37 718	714	0.526	1.83
MgO	$B\ ^1\Sigma^+$ [e]	19 984.0	824.1	0.5822	1.737
MgO	$A\ ^1\Pi_1$ [f]	3 558.6	664.5	0.5054	1.8643
MgO	$X\ ^1\Sigma^+$ [f]	0	785.2	0.5748	1.7482

[a] Ref. [10]. (*Ab initio* calculations)

[b] Ref. [18].

[c] Ref. [13].

[d] This work (see text).

[e] Ref. [6].

[f] Ref. [1].

[g] Preliminary data.

Table 5. Derived spectroscopic constants for $^{24}Mg^{16}O(E\ ^1\Sigma^+)$ from this work. (cm^{-1} unless indicated)

T_e	ω_e	$\omega_e x_e$	B_e	α_e	R_e (Å)
37 718 (± 2)	714.1 (± 0.9)	4.14 (± 0.09)	~0.526[a]	~0.004[a]	~1.83[a]

May change slightly.

[a] See text

References

[1] P. Murtz, H. Thummel, C. Pfelzer and W. Urban, Mol. Phys. 86 (1995) 513.

[2] T. Torring and J. Hoeft, Chem. Phys. Lett. 126 (1986) 477.

[3] Y. Azuma, T. R. Dyke, G. K. Gerke and T. C. Steimle, J. Mol. Spectrosc. 108 (1984) 137.

[4] P. C. F. Ip, K. J. Cross, R. W. Field, J. Rostas, B. Bourguignon and J. McCombie, J. Mol. Spectrosc. 146 (1991), 409.

[5] B. Bourguignon and J. Rostas, J. Mol. Spectrosc. 146 (1991) 437.

[6] K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules, Van Nostrand, New York, 1979.

[7] M. Singh, J. Phys. B, 4 (1971) 565.

[8] S. R. Langhoff, C. W. Bauschlicher, Jr. and H. Partridge, J. Chem. Phys. 84 (1986) 4474.

[9] C. W. Bauschlicher, Jr. and H. Partridge, Chem. Phys. Lett. 205 (1993) 479.

[10] H. Partridge, S. R. Langhoff and C. W. Bauschlicher, Jr., J. Chem. Phys. 84 (1986) 4489.

[11] H. Thummel, R. Kotz and S. D. Peyerimhoff, Chem. Phys. 129 (1989) 129.

[12] A. Antić-Jovanović, V. Bojović, and D.S. Pešić, J. Phys. B., 9 (1976) L575.

[13] D. Bellert, Katherine L. Burns, Nguyen-Thi Van-Oanh, Jinjin Wang, and W. H. Breckenridge, Chem. Phys. Lett. 381(2003) 725.

[14] D. Bellert, Katherine L. Burns, Nguyen-Thi Van-Oanh, Jinjin Wang, and W. H. Breckenridge, Chem. Phys. Lett. 381 (2003) 381.

[15] D. Bellert, K. L. Burns, R. Wampler and W. H. Breckenridge, Chem. Phys. Lett. 322 (2000) 41.

[16] Gerhard Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, Van Nostrand, NewYork, 1950.

[17] Helene Lefebvre-Brion and Robert W. Field, Perturbations in the Spectra of Diatomic Molecules, Academic Press, Orlando, 1986.

[18] Jinjin Wang, D. Bellert, Nguyen-Thi Van-Oanh, and W.H. Breckenridge, to be submitted.

[19] M. Singh, J. Phys. B 6 (1973) 1339.

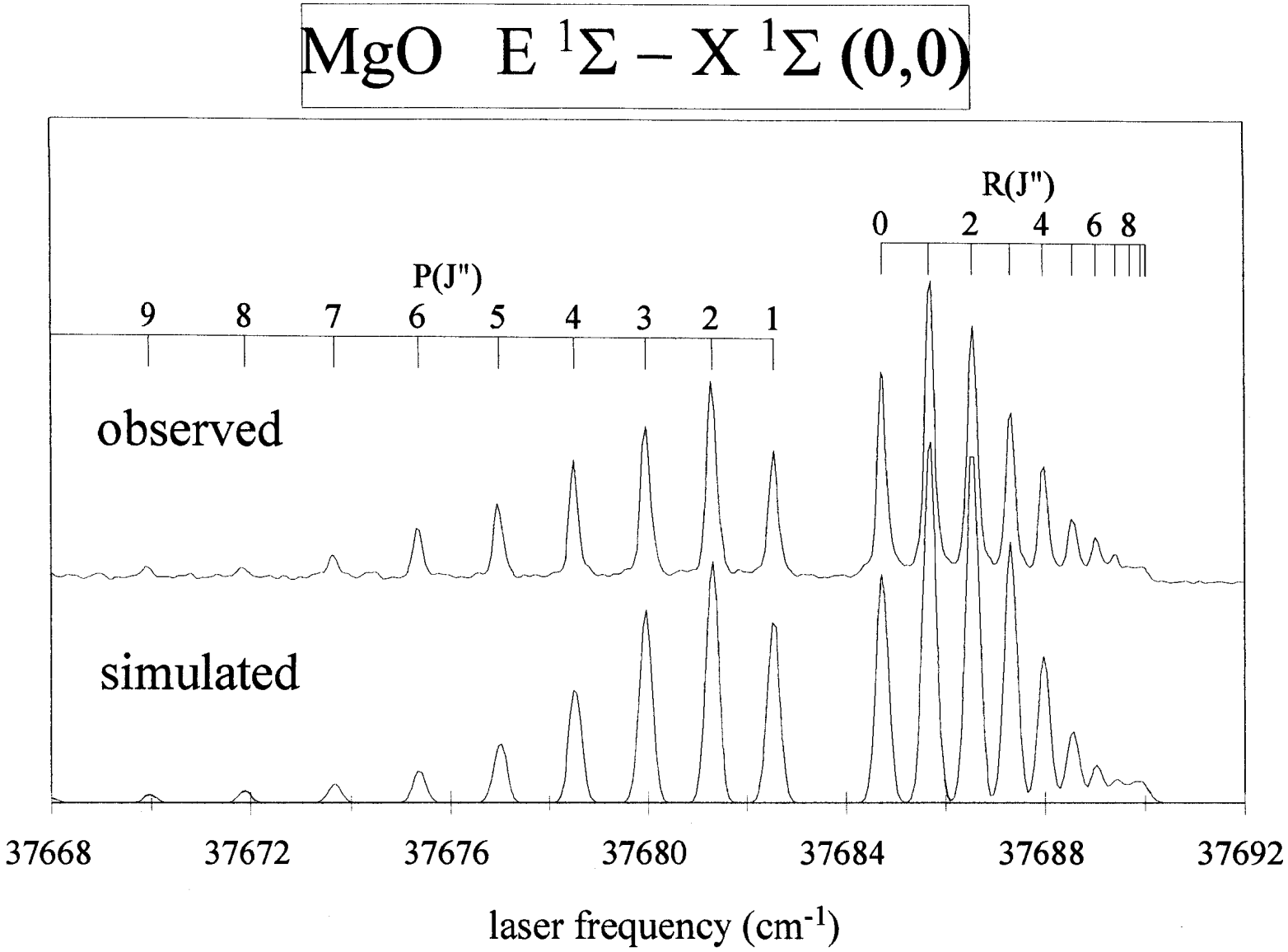
[20] M. Singh, J. Phys. B 6 (1973) 1917.

Figure Captions

Fig. 1 A high-resolution experimental spectrum of the E-X(0,0) transition (top), along with a computer simulation (bottom) with $B''_o = 0.572\ cm^{-1}$, $B'_o = 0.524\ cm^{-1}$, and T = 5 K.

Fig. 2 A Birge-Sponer plot of the $\Delta G_{v'+1/2}$ values in Table II versus $v' + 1$.

Fig. 3 A plot of the $\Delta^2 G_{v'}$ values in Table II (second differences) versus v'.


MgO E $^1\Sigma$ – X $^1\Sigma$ (0,0)
R(J")
0 2 4 6 8
P(J")
9 8 7 6 5 4 3 2 1
observed
simulated
37668 37672 37676 37680 37684 37688 37692
laser frequency (cm^{-1})