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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 $^{24}\text{Mg}^{16}\text{O}$ has been characterized by two-color Resonance-Enhanced Two-Photon Ionization (R2PI) spectroscopy in the $36,000 - 40,000\text{ cm}^{-1}$ region. Several rotationally resolved bands, assigned consistently to $^{24}\text{Mg}^{16}\text{O}(E\ ^1\Sigma^+ \leftarrow X\ ^1\Sigma^+)$ 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 $\sim 50,000 \text{ cm}^{-1}$ in energy. The $X \ ^1\Sigma^+$ ground-state, although formally $\text{Mg}^{+2}\text{O}^{-2}$, in fact appears to have a substantial amount of Mg^+O^- “open-shell” character [8-11]. At much higher energies ($36,000 - 40,000 \text{ cm}^{-1}$), 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 $37,683.5 \text{ cm}^{-1}$ to what is apparently the lowest of these “Rydberg” states, which he tentatively assigned to the $(E \ ^1\Sigma^+ \leftarrow X \ ^1\Sigma^+)\text{MgO} (0,0)$ transition. Antić-Jovanović, *et al.* [12], confirmed the E-X(0,0) assignment of Singh by means of $^{24}\text{Mg}^{16}\text{O}/^{24}\text{Mg}^{18}\text{O}$ 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 $36,000 \text{ cm}^{-1}$ to $40,000 \text{ cm}^{-1}$ 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 $\text{MgO}(X \ ^1\Sigma^+)$ ground-state [1-3], and the third set [14] from vibrational levels of the lowest-lying metastable triplet

state, $\text{MgO}(a^3\Pi_2)$ [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 $^{24}\text{Mg}^{16}\text{O}$ 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 Molelectron 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 $\sim 5 \times 10^{-5}$ 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. 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 $\pm 0.002 \text{ cm}^{-1}$ 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 $\Omega = 1$. 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 $\Omega = 1$ 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 $\Delta^2 G_{v'}$ (2nd 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 $\omega_e'' = 785.7 \pm 0.5 \text{ cm}^{-1}$ and $\omega_e x_e'' = 5.33 \pm 0.30 \text{ cm}^{-1}$.) 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, $\omega_e' = 714.1 \pm 0.9 \text{ cm}^{-1}$ and $\omega_e x_e' = 4.14 \pm 0.09 \text{ cm}^{-1}$ **[new values to be provided by Marc-Andre]** for the $E(^1\Sigma^+)$ state of $^{24}\text{Mg}^{16}\text{O}$. 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 $\Delta^2 G_{v'}$ (2nd 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 $v' \leq 7$.

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 ($q \leq 0.0001 \text{ cm}^{-1}$), 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 $\sim 0.01 \text{ cm}^{-1}$.

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 $\Omega = 1(e)$ levels and the $\Omega = 0^+(e)$ 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 $B'_0 = 0.524 \text{ cm}^{-1}$ 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):

$$B_v = B_e - \alpha_e(v + 1/2) \quad (1)$$

$$\alpha_e (\text{Morse curve}) = \frac{6[(\omega_e x_e)(B_e)^3]^{1/2}}{\omega_e} - \frac{6(B_e)^2}{\omega_e} \quad (2)$$

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 $B'_0 = 0.524$ 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'_0 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 $\sim 0.018 \text{ cm}^{-1}$ 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 “ $\Omega = 1$ ” levels, although the $^3\Sigma$ states are formally “case b,” where Ω is not really a good quantum number). The *ab initio* calculations of Peyerimhoff 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 $\Omega = 1$ 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 O^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 $R \approx 2.7\text{ \AA}$ and $R \approx 4.5\text{ \AA}$ in addition to the absolute minimum at 1.8 \AA . 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 $\sim 0.2 \text{ cm}^{-1}$. 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 $^1\Sigma^+(v' = 0-5)$ vibrational levels, and will be difficult to characterize experimentally.]

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

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

Band	Band Origin Wavenumber ($\pm 0.5 \text{ cm}^{-1}$)	$B'_v (\pm 0.003)$	$B''_v (\pm 0.002)$
(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 ± 0.007^c	0.570 ± 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'	$E_{v'} (\text{cm}^{-1}) (\pm 0.3 \text{ cm}^{-1})$	$\Delta G_{v'+1/2} (\text{cm}^{-1})$	$\Delta^2 G_{v'} (\text{cm}^{-1})$
0	37 683.6		
1	38 388.5	704.9	7.6
2	39 085.8	697.3	6.2
3	39 776.9	691.1	11.0
4	40 457.0	680.1	6.7
5	41 130.6	673.6	10.3
6	41 793.9	663.3	7.9
7	42 449.3	655.4	

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 $B_0 = 0.524 \text{ cm}^{-1}$ and using the Pekeris relationship (eq. 2) for a Morse curve, with $\omega_e = 714.1 \text{ cm}^{-1}$ and $\omega_e x_e = 4.14 \text{ cm}^{-1}$, to calculate $\alpha_e = 4.2 \times 10^{-3}$. **May change slightly**

^b $B_v(\text{exptl.}) - B_v(\text{predicted}) = q$ (see text)

^c Ref. [7].

^d From low signal-to-noise data.

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

Species	Electronic State	T_e (cm^{-1})	ω_e (cm^{-1})	B_e (cm^{-1})	R_e (\AA)
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 $^{24}\text{Mg}^{16}\text{O}(\text{E } ^1\Sigma^+)$ from this work. (cm^{-1} unless indicated)

T_e	ω_e	$\omega_e x_e$	B_e	α_e	$R_e (\text{\AA})$
37 718 (± 2)	714.1 (± 0.9)	4.14 (± 0.09)	$\sim 0.526^a$	$\sim 0.004^a$	$\sim 1.83^a$

May change slightly.

^a See text

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Figure Captions

Fig. 1 A high-resolution experimental spectrum of the E-X(0,0) transition (top), along with a computer simulation (bottom) with $B''_0 = 0.572 \text{ cm}^{-1}$, $B'_0 = 0.524 \text{ cm}^{-1}$, and $T = 5 \text{ K}$.

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 ¹Σ – X ¹Σ (0,0)

