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Experimental studies of the 200 nm diffuse band in zinc vapours and its interpretation

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Abstract. The absorption spectrum of zinc vapours is measured under various conditions in the 190-224 nm region and the absolute absorption coefficient per one pair of atoms is derived. A relatively narrow diffuse band at 200.22 nm (in a vacuum) is observed and its profile is carefully determined for several temperatures. It is found that the band maximum slightly decreases with a temperature increase. This indicates that the band is generated by transitions occurring within the range of negative energy values of the ground state potential.

The experimental results are utilized for deriving some information concerning the upper state potential and the oscillator strength function via semiclassical calculations of the band profile and its comparison with the experimental one. It is shown that theoretical potentials for the lowest Rydberg states available cannot be responsible for the band formation and some part of the previously unknown excited state potential near its minimum as well as the $f(R)$ function reproducing the experimental band profile are found. The equilibrium position, R_e , and the energy minimum, $E(R_e)$, for this state are established to be $3.94 \pm 0.15 \text{ \AA}$ and $49660 \pm 50 \text{ cm}^{-1}$, respectively. It is also shown that the $f(R)$, being equal to zero at large distances, for R lower than about $4 \text{ \AA}$ increases rapidly to the maximal value of 0.61 ± 0.03 at $R = 3.65 \pm 0.05 \text{ \AA}$. Such a behaviour indicates that the upper state here can be coupled with a state characterized by strongly allowed transition to the ground state. Discussion concerning this matter and identification of the upper state asymptote is presented.

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1. Introduction

In our previous paper [1], devoted to the experimental and theoretical studies of the blue satellite of the Zn ($4^1P_1 - 4^1S_0$) 213.8 nm line, the observation of the diffuse band appearing in the far UV region near 200 nm was reported. The present work being a continuation of those studies is aimed at deriving more experimental data concerning this band, hereafter referred to as the S2 band following [1]. The problem is important because, to our knowledge, the S2 band seems to be hitherto the only observed spectral feature which can provide information on the electronic transition in Zn_2 between its ground state and the poorly known excited states lying above the $1_u(^1\Pi_u)$ state of the ($4^1P_1 + 4^1S_0$) asymptote (see figure 5 in section 3).

It should be mentioned that although several UV diffuse bands in dense vapours of the zinc family elements have been discovered as early as in the 1920s [2 - 4] the origin of the S2 band has not

been unambiguously established. Most frequently it has been suggested that the upper electronic state for this band is one of the lowest Rydberg states $^1\Sigma_u^+$ or $^3\Sigma_u^+$ correlated with, respectively, the $((n+1)^1S_0 + n^1S_0)$ [4] or the $((n+1)^3S_1 + n^1S_0)$ [5] atomic asymptote, where $n = 6, 5, 4$ for Hg, Cd, Zn. This hypothesis, unfortunately, has never been verified because potential energy curves of so highly excited states, in particular for Cd and Zn, were missing.

We have recently carried out the first quantitative studies of such a band in cadmium [6, 7] where it appears at about 212.5 nm. The spectroscopic measurements were performed in fluorescence and absorption and from the temperature variation of the band profile in the later case, some part of the upper state interaction potential was derived and the oscillator strength function for the involved transition was roughly estimated. On the other hand Czuchaj et al. have calculated interaction potentials for several electronic states of Cd_2 [8] and Zn_2 [9] including, for the first time, both above mentioned Rydberg states. It is noteworthy, that lower valence states predicted by those authors reproduce the known spectral features much better than other existing theoretical potentials as it was discussed in [1]. Contrary to this, a comparison of the experimental findings for Cd_2 [7] with the theoretical potentials for the Rydberg $^1\Sigma_u^+(6^1S_0)$ and $^3\Sigma_u^+(6^3S_1)$ states from [8] showed qualitative disagreement indicating that neither of these states can be a carrier for the S2 band.

The present studies were undertaken to examine this problem in zinc what would be an additional test for the S2 band interpretation. The experimental study of the S2 band for this element is, unfortunately, more difficult than in cadmium, not only in the case of conventional spectroscopy but with the new techniques as well. The main difficulties arise from the higher melting point for Zn, resulting in the necessity of work at temperatures of about 1000 K or more to detect this rather weak band, as well as from the inconvenient spectral region where the band appears. Thus, although the great interest in the electronic structure of the group 12 diatomic systems has been observed since several years [10] the S2 band of Zn_2 has not been studied as yet.

2. Experimental details and results

The apparatus and procedure were generally the same as those described in [1]. Therefore, only those improvements that are important to the present investigation are described below.

Two quartz (suprasil) cells, 5 and 25 cm in length and 3 cm in diameter, containing the high purity (6n) zinc, distilled into relatively short side arms, were prepared. The shorter cell was used for the precise, quantitative determination of the wings profile of the 213.8 nm Zn line, utilized for an intensity calibration of the much weaker spectrum extended towards short wavelengths including the S2 band which was measured with the longer cell.

In order to eliminate the so-called hot Schumann-Runge (S-R) bands of the O_2 molecule [11] whose intensity strongly depends on temperature [12], the oven for heating the cell was flushed by a regulated argon flow as it was established in [1]. The gas was fed through two quartz narrow pipes in

which it was heated to the oven temperature in order to minimize its influence on the thermal conditions inside the oven.

The high resolution Rowland spectrometer with a 6 m concave grating was used as a dispersive system. The great luminosity of this device in the UV region and a long optical path inside the spectrometer (~ 12 m) resulted in the detection of a very weak atmospheric O_2 absorption originating from the lowest vibrational level in the ground state potential of this molecule. This spectrum was then used to improve the wavelength calibration of the spectrometer in the far UV region where several rotational lines of the 2-0 and 1-0 ro-vibronic S-R band systems were observed as shown in figure 1. The J assignment here was adopted after [13] and very accurate vacuum wavelengths of the particular lines were taken from [14].

Although our concern in this work was with the S2 diffuse band near 200 nm, for an accurate intensity calibration the spectra were determined over a much broader spectral range, between about 199 – 224 nm, including the wings of the Zn 213.8 nm resonance line. The measured quantity was the absorption coefficient of the Zn vapour as a function of the relative frequency

$$k(\Delta\nu) = \frac{-\ln[I(\Delta\nu)/I_0(\Delta\nu)]}{d} \quad (1)$$

Here $\Delta\nu = \nu - \nu_0$, with ν_0 being a frequency of the line centre assumed as 46745.37 cm^{-1} [15] (here and hereafter the frequency, ν , is measured in cm^{-1}), d is the cell length, and $I(\Delta\nu)$ and $I_0(\Delta\nu)$ are the signal amplitudes measured for Zn vapour and empty cell, respectively, normalized to their values at the same $\Delta\nu$ chosen in the region free of any absorption.

In view of the main goal of the present work, we have concentrated on possibly precise determination of the absolute (reduced) absorption coefficient per one pair of atoms

$$k^{(r)}(\Delta\nu) = k(\Delta\nu)/N^2 \quad (2)$$

where N is the vapour number density. This value is usually calculated from the ideal gas law using an appropriate formula for the relation between the pressure (p) of the saturated vapour and the measured temperature (T_s). Such a method, however, proved to be insufficiently accurate in the case of the longer cell due to the considerable temperature gradient along its side arm and the cell body. Therefore, the intensity calibration of the spectrum under study at the given mean temperature ($T \pm 5$ K) of this cell was achieved by its comparison and adjusting to a suitable spectrum of the reduced absorption coefficient in the wings of the resonance 213.8 nm line, determined much more precisely for the short cell. In this case the cell together with its Zn reservoir occupied the central part of the 60 cm long oven where the temperature was well established and measured with accuracy of 0.2 K. The saturated vapour pressure in this case was calculated from $p(T_s)$ curve received via a least square fit to sufficiently accurate vapour pressure measurements recommended by Nesmeyanov [16] and Hultgren et al. [17]. Fortunately, over the temperature range about 900 – 1000 K a considerable number of such data exists and they do not show a great scattering of values, thus, the relative pressure error generated

by that formula is estimated as 3 per cent yielding the uncertainty in the absolute absorption coefficient derived for the short cell not greater than 6 per cent.

Using the above method the absolute absorption coefficient spectrum, given by equation (2), for unsaturated vapour of the densities between about $(2.5 - 9.1) \times 10^{17} \text{ cm}^{-3}$ was determined at several cell temperatures between about 940 – 1030 K. These limitations were due to increasing influence of the atmospheric O_2 absorption for lower N and increasing instability of measurements at higher temperatures. In any case, the cell temperature T was appreciably higher than T_s determining the vapour density.

The measurements showed that even for so high vapour density as of the order of 10^{18} cm^{-3} the band under study is a relatively narrow continuum of nearly symmetric profile, well isolated from the blue satellite of the 213.8 nm line, S1, as it is seen in figure 2. Intensity of both bands presented somewhat decreases with a temperature increase, however in the case of the S2 band this effect seems to be slightly enhanced by influence of the O_2 (1-0) band system which gives a constant contribution to the Zn vapour absorption under study.

In order to determine accurately the temperature dependence of the S2 band, being very important for its interpretation in terms of the interaction potentials, it was necessary to remove the contribution from molecular oxygen. Because it was impossible to do this accurately for the total band profile we have decided to estimate the temperature effect only for the band centre. This was done by fitting the Gaussian profile, $G(\lambda)$, to the particular, experimentally derived spectrum as it is presented in figure 3. For the sake of comparison with figure 1, the spectrum is here plotted as a function of the vacuum wavelength (λ_v). It was assumed that the optimal fitting is reached when the difference between the experimental spectrum and the fitted profile does not depend of the Zn vapour density and agrees reasonably well with that of the O_2 (1-0) band spectrum.

It is noteworthy, that all the experimental spectra could be fitted by the $G(\lambda)$ profile of the same width $\Gamma = 0.755(5) \text{ nm}$ (FWHM) and the centre position $\lambda_0 = 200.220(5) \text{ nm}$ (or, alternatively, $\Gamma = 190(5) \text{ cm}^{-1}$ and $\nu_0 = 49945(2) \text{ cm}^{-1}$) while its maximum $G(\lambda_0)$ depended on the square of the Zn vapour density with rather moderate scatter of values. In such a way $k^{(r)}(\lambda_0) \equiv G(\lambda_0)/N^2$ for different cell temperatures, which represents the pure temperature effect for the band maximum, was determined and presented in figure 4. It is seen that, in spite of considerable errors originating mainly from the vapour density uncertainty mentioned above, the reduced absorption coefficient in the maximum of the S2 band, $k^{(r)}(\lambda_0)$, clearly decreases with a temperature increase.

Since the temperature dependence of a thermally averaged absorption spectrum arises from a population of different scattering states (free states) in the ground state potential, $V_g(R)$, and is roughly described by the Boltzmann distribution as $\exp(-V_g(R(\Delta\nu))/k_B T)$, the effect observed for the S2 band maximum indicates that this band is formed by transitions originating mainly in the region of negative values of the ground state potential, i.e. within its well, similarly as it was observed for the analogical Cd_2 band in [6,7]. A slope of the straight line fitted to the data in figure 4 yields the ground state

potential in the band maximum amounting to $360 \pm 150 \text{ cm}^{-1}$ which seems to be reasonable accounting for appreciable errors of the experimental data and rather narrow range of temperature explored.

3. The band interpretation

Taking into account the experimental findings presented in section 2, some information concerning the S2 band origin can be deduced.

In particular, the shape of the band is typical for thermally averaged spectral features associated with asymptotically forbidden transitions that have been observed in the past for different diatomic systems (see e.g. [18, 19] and interpreted in a frame of the quasimolecular theory of spectral line wings and satellites associated with optical collisions. This theory, comprehensively discussed in [20], is particularly useful in its classical quasistatic limit, which straightforwardly leads to the well-known inversion technique developed for both the asymptotically allowed [21] and forbidden [22-24] electronic transitions. The method, based on analysis of the temperature dependence of the spectrum, has been successfully used by many authors for deriving the interaction potentials and the transition moment function involved. A review of these results may be found in [20].

In the case of the Zn_2 band studied in this work such a method could not be fully utilized because the sufficiently accurate temperature dependence of the total band profile was hardly attainable. However, it was possible to employ the experimental profile for verification of various potential energy curves assumed for the upper state responsible for the band formation. Looking for the suitable candidate we have considered both of the lowest Rydberg states from [9], referred to as $\text{R}3(^3\Sigma_u^+)$ and $\text{R}1(^1\Sigma_u^+)$ in figure 5, as well as the hypothetical highly excited $\text{Y}(\Lambda_u)$ state of the equilibrium distance close to one of the ground state potential well from [9].

The calculation of the band profile were, in general, performed using the well known semiclassical Szudy and Baylis formula [25, 20]. According to this approach the adiabatic line wing profile associated with an electronic transition between the lower (l) and the upper (u) state, characterized by the respective potential energy curves $V_l(R)$ and $V_u(R)$ of the homonuclear diatomic system, in the case of absorption is given by

$$k(\Delta\nu) = N^2 \frac{4\pi^2 e^2}{mc^2} \frac{g_\Omega}{g_J} \sum_c f(R_c) R_c^2 \cdot \frac{\exp(-V_l(R_c)/k_B T)}{\Delta V'(R_c)} |36\pi z_c|^{1/2} L(z_c) \quad (3)$$

with

$$z_c = \frac{1}{2} \left(\frac{\mu c^2}{k_B T} \right)^{1/3} (\Delta V'(R_c))^2 |\Delta V''(R_c)|^{-4/3} \quad (3a)$$

where $\Delta\nu$ and ΔV are expressed in cm^{-1} .

In the above equations e , m , c and k_B have their usual meanings, g_Ω and g_J are the statistical weights of the excited molecular and parent atomic state, $f(R_c)$ is the oscillator strength at the internuclear separation R_c , μ is the reduced mass and $L(z_c)$ is the universal line shape function defined in [25].

The subscript c denotes the so-called Condon points at which the separation R_c satisfies the equation:

$$h\Delta\nu = \Delta V(R_c) \equiv V_u(R_c) - V_l(R_c).$$

Only the real Condon points were accounted for and all calculations of the band profile were performed for the temperature of 1031 K at which the experimental spectrum, being derived for high vapour density, was practically unaffected by the oxygen molecule $\nu'' = 0$ bands.

The Zn_2 potential energy curves of higher excited states available from [9] are presented in figure 5. This figure also shows that the potential differences between the ground state (X) and each excited state (R1, R3) have a monotonic character, so that in both cases there is only one Condon point R_c for each $\Delta\nu$. In such a situation the semiclassical profile given by Eqs. (3) simplifies to the classical quasistatic one and for the reduced absorption coefficient we have

$$k^{(r)}(\Delta\nu) = \frac{4\pi^2 e^2}{mc^2} \frac{g_\Omega}{g_J} f(R_c) R_c^2 \cdot \frac{\exp(-V_l(R_c)/k_B T)}{\Delta V'(R_c)} \quad (4)$$

It is noteworthy that this simple classical wing profile was verified via quantum-mechanical calculation and found a quite adequate in the case of the monotonic difference potentials i.e. far from any extremum of $\Delta V(R)$ (see e.g. [26]).

For the R1 excited state both statistical weights are equal to 1 and $f(R_c)$ can be deduced from an electric dipole moment function for the $\text{R1} \leftarrow \text{X}$ transition obtained also in [9]. Although due to the character of the $\Delta V(R)$ curve any band for this transition is expected, the shape of the $f(R)$ function (see inset of figure 5) leads to an appearance of the weak diffuse band in the far wing of the $5^1\text{S}_1 - 4^1\text{S}_0$ atomic line, as shown in figure 6. The predicted position of the calculated band agrees surprisingly well with experimental data, however, the intensity is about a hundred times weaker and the width of band is much more larger. So big disagreement proves clearly that the interaction data used here can not be responsible for the S2 band generation.

For the $\text{R3} \leftarrow \text{X}$ transition, a transition moment function is not available. However, from Eq. (4) through its inversion one can provide the oscillator strength which together with responsible potentials could reproduce the experimental band profile $k^{(r)}(\Delta\nu)$. It is give by

$$f(R) = C \frac{g_J}{g_\Omega} k^{(r)}(\Delta\nu(R)) \frac{\Delta V'(R)}{R^2} \exp(k_B T / V_g(R)) \quad (5)$$

where C includes all the constant factors and for $k^{(r)}$ in cm^5 , $\Delta\nu$ in cm^{-1} and R in $\text{\AA}$ it amounts to $8.988937 \times 10^{-2} \text{ cm}^{-1}$.

Unfortunately, this formula, for theoretical potentials $V_3(^3\Sigma_u^+)$ and $V_g(\Sigma_u^+)$ from [9] and the statistical weights of both states amounting 3, for $\Delta\nu$ related to the frequency $\nu_0 = 53672.24 \text{ cm}^{-1}$ of the $5^3\text{S}_1 - 4^1\text{S}_0$ atomic transition [15] gives unreasonably high f -values of about 5 at the band maximum. Therefore, we conclude that the R3 molecular state from [9], also can not be a carrier of the S2 band.

Finally, we have considered the excited state of the ungerade symmetry, $\text{Y}(\Lambda_u)$, for which the potential difference, $\Delta V(R)$, is not a monotonic function but it has a minimum for the energy roughly

determined by the S2 band spectral position at separation close to one for the ground state potential from [9]. In such a situation it can be expected that the band observed is the so-called rainbow satellite appearing in the red wing of any forbidden line of the frequency determined by an atomic asymptote of the $Y(\Lambda_u)$ state. Because the shape of the band calculated depends only on derivatives of the difference potential (see Eqs. 3) it is not necessary to assume any real state for this asymptote.

For some simplicity of calculations, the part of this $\Delta V(R)$ curve which could be responsible for the formation of the S2 band was approximated with the quadratic function and $f(R)$ was assumed as a Gaussian of two different slopes. Several combinations of such interaction data were tested receiving finally quite good agreement between the calculated quasiclassical band profile (the antistatic part was omitted) and the experimental one as it is presented in figure 7. The profile calculated for $f(R) = \text{const}$, normalized to the maximum of the experimental band, is also shown in this figure. Although in this case the spectrum calculated shows a distinct band the experimental profile can be reproduced only for the $f(R)$ function which is different from zero in a relatively narrow range of the internuclear separation. The part of the difference potential curve, ΔV , and $f(R)$ for the X-Y transition used for the calculation of spectra from figure 7 are presented in figure 8. Numerical values for the difference potential over limited range of R (as shown) are given by parabola $aR^2 + bR + C$ with $a=1299.282$, $b=-10126.55$, $c=69608.7$. The upper state potential curve $Y(\Lambda_u)$ is found as a sum of this $\Delta V(R)$ and $V_g(R)$. It is seen that the minimum of the upper state appears just above the maximum of the barrier in the ${}^1\Pi_u$ (${}^1P + {}^1S$) state producing the diffuse band S1 and that the X-Y transition being forbidden at large separations becomes allowed at distances close to the minimum of the upper state potential. These results indicate that the $Y(\Lambda_u)$ state can be here coupled with a state characterized by strongly allowed transition to the ground state.

Systematic tests were made for possible variations in the calculated band profile due to variations of the position and value of the $\Delta V(R)$ minimum and the $f(R)$ maximum. Accounting for the results of these tests the main parameters for the $Y(\Lambda_u)$ state i.e. the equilibrium position R_e and the $V(R_e)$ energy are derived to be 3.94 ± 0.15 Å and 49660 ± 50 cm⁻¹ respectively, with $f(R)$ having a quite reasonable maximal value of 0.61 ± 0.03 at $R = 3.65 \pm 0.05$ Å. The error bounds for the upper state are estimated taking into account also the ground state potential uncertainty.

4. Discussion

The existence of highly excited states with a minimum immediately above the barrier in the ${}^1\Pi_u$ (${}^1P + {}^1S$) state have been suggested in the earlier less sophisticated ab initio calculations of the electronic structure of the Group II (A and B) metal diatomic molecules [27-31]. For Zn_2 such a state was first predicted by Hay et al. [27, 28] who have shown the important effects in the excited valence potential energy curves arising from the $Zn^+({}^2S) + Zn^-({}^2P)$ ion pair states although they are asymptotically unstable. In particular, the ${}^1\Pi_u$ diabatic ion pair state which is strongly attractive at relatively long distances dramatically changes the originally repulsive lower states of the same symmetry due to an

avoided crossing. It deals, in particular, with the $^1\Pi_u$ state of the asymptote $^3P + ^3P$ and the lower $^1\Pi_u$ state correlated with the $^1P + ^1S$ which, finally, become attractive at smaller R as a result of mixing with that ion-pair state. In this way the resulting $^1\Pi_u(^3P + ^3P)$ adiabatic state has a potential well close above the barrier in the $^1\Pi_u(^1P + ^1S)$ adiabatic state.

More recently, Ellingsen et al. [32] have performed all electron calculations of the ground state and the eight lowest-lying excited states of Zn_2 at several levels of theory including spin-orbit coupling. Those calculations, among other results, also showed that the $1_u(^1\Pi_u) (^1P + ^1S)$ state is perturbed by the interaction with the $1_u(^1\Pi_u)$ state dissociating to the $^3P + ^3P$. The resulting avoided crossing yielded the barrier of about 5600 cm^{-1} in the $1_u(^1\Pi_u) (^1P + ^1S)$ state and the well depth of about 9600 cm^{-1} in the $1_u(^1\Pi_u) (^3P + ^3P)$ state.

Assuming that the $1_u(^1\Pi_u) (^3P + ^3P)$ state of the asymptotic energy of $2 \times 32696.34\text{ cm}^{-1}$ is the upper state for the S2 band under study, its spectral position should be expected at about 56000 cm^{-1} whereas it is observed at 49945 cm^{-1} . Moreover, the transition between the $1_u(^1\Pi_u) (^3P + ^3P)$ and ground states at long distances is fully allowed that disagrees with the present situation.

Unfortunately, the above mentioned early calculations according to their authors opinion, could not provide any data concerning the Rydberg states of interest because of limitations of the basis set being inadequate for describing such states. However, the van der Waals coefficients, describing long-range interactions for the R1 and R3 states were calculated by Ellingsen et al. [33] and proved to be very large. This indicates that these states can be more attractive than those received by Czuchaj so, if the spin-orbit interaction (not considered in [9]) is taken into account, the potential energy curve for the 1_u fine structure components of the adiabatic R3 state can undergo the avoided crossing with the $1_u(^1\Pi_u) (^1P + ^1S)$ excited state. Hence, the here postulated Y state would be attributed to the $1_u(^3\Sigma_u^+)$ Rydberg state of the $Zn(5^3S_1 + 4^1S_0)$ asymptote. The well depth of this state would be then estimated as about 4000 cm^{-1} .

The above conclusion is consistent with that inferred in [7] for the S2 band interpretation in Cd_2 . Moreover, basing on the combining results of that paper with findings derived from the extensive studies of fluorescence spectra of the Cd vapour following strong laser excitation [6, 34], in [7] we have argued that the $1_u(^3\Sigma_u^+)$ state could be the state of the double minimum and the interaction data received from the S2 band analysis deal with its outer well. This suggestion need further theoretical studies of the electronic structure of the zinc family diatomic systems, particularly in highly excited valence and Rydberg states among which several avoided crossings one can expect. The adequate description of these states over wide range of separations requires the knowledge of states arising from higher-lying asymptotes which are not yet available.

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Figure captions

Figure 1. The atmospheric O₂ absorption spectrum observed at room temperature.

Figure 2. The reduced absorption coefficient in the far blue wing of the self-broadened Zn 213.8 nm line including its satellite band, S1, and the S2 band measured during the same scan. The spectra were derived at different temperatures: —, T = 983 K; ···· T = 1031 K.

Figure 3. The absorption coefficient of the S2 band observed at $N = 8.2246 \times 10^{17} \text{ cm}^{-3}$ and $T = 1023 \text{ K}$ (upper plot) in comparison with the one derived for an empty cell at room temperature scanned in smaller step (lower plot). The upper smoothed contour represents a Gaussian profile of the parameters: $G(\lambda_0) = 0.087 \text{ cm}^{-1}$, $\lambda_0 = 200.22 \text{ nm}$, $\Gamma = 0.75 \text{ nm}$. (For particular description see the text)

Figure 4. Temperature dependence of the reduced absorption coefficient in the S2 band center.

Figure 5. Theoretical potential energy curves of Zn₂ for the ground state, X, and ungerade excited states correlated with higher atomic asymptotes from Ref. [9]. Dashed curves represent respective difference potentials. The oscillator strength function for the transition R1-X is presented in the inset.

Figure 6. The reduced absorption coefficient as a function of difference frequency for the R1-X transition. The comparison of the experimental spectrum, (••), with this calculated multiplied by 100, (—), using the suitable potentials and $f(R)$ function presented in figure 5. The dashes curve represents the spectrum calculated for $f(R) = 1$.

Figure 7. The comparison of the experimental (°°°) S2 band profile with the calculated ones (—) using the difference potential $\Delta V(R)$ and the $f(R)$ function presented in figure 8. The dashes curve represents the spectrum calculated for $f(R) = \text{const}$ resulting from normalization of the band maximum to the experimental intensity.

Figure 8. The established part of the difference potential energy curve, ΔV , responsible for the S2 band formation and the respective excited state potential, $Y(\Lambda_u)$. The oscillator strength function for the transition X-Y is presented in the inset. The potential energy curve of the lower close-lying 1_u ($^1\Pi_u$) state dissociating to ($4^1P_1 + 4^1S_0$) is also presented.

Figure 1 (gryc0430/figure1.tif)

Figure 2 (gryc0430/figure2.tif)

Figure 3 (gryc0430/figure3.tif)

Figure 4 (gryc0430/figure4.tif)

Figure 5 (gryc0430/figure5.tif)

Figure 6 (gryc0430/figure6.tif)

Figure 7 (gryc0430/figure7.tif)

Figure 8 (gryc0430/figure8.tif)