

## Determination of Potential Curves of Br<sub>2</sub> in Franck-Condon's Region (Penentuan Potensi Lengkung Br<sub>2</sub> di Rantau Franck-Condon)

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### ABSTRACT

The extinction of Br<sub>2</sub> molecules in gas state is measured for different wavelengths of incident light in interval of 370 – 570 nm by method of gas spectroscopy. The measurement is made on the basis of Franck-Condon's principle, under which a transition to a more excited state is done without changing the intercore distance (in further text, R). The graph of energy dependence on extinction is drawn. On the graph are recognized two Gausses slopes and their separation (deconvolution) is done. The complete Gausses functions are determined on graph. The method of mirror symmetry is applied on Gausses slopes of extinction and symmetrical extinction values (Es) are obtained. Borders of Franck-Condon's area are determined from ground state of Linear Harmonic Oscillator (LHO). Tables of dependence on R and the excitation energy are given. On the basis of these tables are drawn potential curves of electron energy E(R) in excited electronic states of Br<sub>2</sub> molecules as functions of R in Franck-Condon's area.

Keywords: Br<sub>2</sub>; extinction; Franck-Condon's region; intercore distance; potential curve

### ABSTRAK

Kepunahan molekul Br<sub>2</sub> dalam keadaan gas diukur dengan jarak gelombang yang berbeza cahaya tuju dalam tempoh daripada 370-570 nm dengan menggunakan kaedah gas spektroskopi. Pengukuran ini dibuat berdasarkan prinsip Franck-Condon dengan peralihan kepada keadaan teruja dilakukan tanpa menukar jarak antara teras (dalam teks seterusnya, R). Graf tenaga pergantungan kepada kepunahan dilukis. Di dalam graf tersebut, dua cerun Gausses dan pemisahan mereka (deconvolution) dilakukan. Fungsi Gausses yang lengkap ditentukan pada graf. Kaedah cermin simetri digunakan pada cerun Gausses kepunahan dan nilai kepunahan simetri (Es) diperolehi. Kawasan sempadan Franck-Condon ditentukan daripada keadaan asas Pengayun Harmonik Linear (LHO). Jadual pergantungan R dan tenaga pengujaan diberi. Berdasarkan jadual ini, lengkung potensi tenaga elektron E(R) akan dilukis dalam keadaan elektronik teruja molekul Br<sub>2</sub> sebagai fungsi R di kawasan Franck-Condon.

Kata kunci: Br<sub>2</sub>; jarak antara teras; kepunahan; potensi lengkung; rantau Franck-Condon

### INTRODUCTION

Methods for computing the vibrational turning points of diatomic molecules are summarized in research (Coxon 1971). Available spectroscopic data have been used to determine the potential energy curves for the  $^1\Sigma_g^+$  and  $B^3\Pi_{0+u}$  vibrational states using extension of technique given by Vanderslice et al.

The total energy of the molecules (except for the spin and magnetic interactions) is equal to the sum of kinetic and potential energy of nuclei and electrons. The energy of electrons depends on R as a parameter. The dependence of potential energy on R is described by curve of potential energy of electronic state of molecule or that is equivalent by curve of potential. According to the principle of minimum of energy, if potential curve have minimum, a stabile state of molecule is possible.

In his paper, Coxon (1972), described semi empirical method for extrapolation rotational constants to the potential minimum of Br<sub>2</sub>. Franck-Condon factors for the  $^1\Sigma_g^+$  system of Br<sup>79</sup>Br<sup>81</sup> are reported for the ranges of vibrational quantum number 0|v''|23, 0|v'|28.

Classical investigations of the discrete absorption spectrum of halogen spectrum of halogen molecules, especially Br<sub>2</sub> and I<sub>2</sub>, have resulted in the accurate identification of transitions between specific vibrational and rotational levels of these diatomics (Linderman et al. 1979). Such analyses have permitted the precise characterization of the potential curves for the bound  $X^1\Sigma_g^+$  ground and  $B^3\Pi_{0+u}$  excited states.

Li and Balasubramanian (1989) calculated the spectroscopic properties and potential curves of I<sub>2</sub> by the complete active space SCF method followed by the interaction (CI) and recent relativistic many-body perturbation methods. Teichteil and Pelissier (1994) calculated the potential curves of I<sub>2</sub> with an *ab initio* relativistic atomic pseudo-potential method and analyzed the available experimental data. Asano and Yobushita (2003) calculated the potential curves of I<sub>2</sub> by the spin-orbit configuration interaction (SOC) method.

In this paper, the results and method of direct measuring of extinction of Br<sub>2</sub> molecules in gas state are given. Measuring data and graph of energy dependence

on extinction are analysed with computer software Origin. Borders of Franck-Condon's area are recognized and potential curves of ground state  $^1\Sigma_g^+$  for  $\text{Br}_2$  are drawn.

#### SUBJECT & METHODS

The simple harmonic oscillator has a parabolic potential and the molecule's energy can rise indefinitely. A better model for the potential energy of a diatomic molecule is Morse potential, because in the Morse potential (Morse 1929), the molecule can dissociate if its vibrations get too large. At small vibrational energies, the molecule remains constrained within the potential energy well. However at large values of  $R$ , the energy levels off, at the dissociation energy.

The dissociation energy,  $D_e$ , is defined as the energy necessary to dissociate the molecule when measured from the bottom of the potential energy well. The ground state and each excited state have their own individual Morse curves. These curves have different dissociation energies, equilibrium bond lengths and curvature (Barrow 1962).

#### THEORETICAL BACKGROUND OF EXPERIMENT

Adiabatic approximation approximates quantum system with composition of two subsystems in which one is slow and the other is fast. In case of slow system molecules consists of cores, while fast one consists of fast electrons. Approximation of slow system with immovable one is Born-Openhajmer's or Born's approximation. Orbital part of Hamiltonian (spin and spin-orbital part are ignored) has kinetic energy of electrons and potential energy due to Coulomb interaction electron-electrons and electron-cores:

$$\hat{H}_{el} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{k,i} \frac{Z_k e^2}{4\pi\epsilon_0 R_{ik}}, \quad (1)$$

where  $i$  and  $j$  count electrones,  $k$  counts cores, and  $R_{ik}$  in accordance with Born's approximation is constant. Therefore, we only observe electronic subsystem, separated in accordance with the adiabatic approximation in potential determined by Born's approximation. Spin state of electrons are not counted. Born's approximation separates movements of electrons from movements of cores.

The result of Born's approximation is representing energy of molecules as sum of electronic, vibrational and rotational energy.

$$E = E_\theta + E_v + E_r, \quad (2)$$

In spectroscopy, the above approach is acceptable due to distinct three classes of molecular spectra; rotational, vibrational and electronical. Spectroscopic data on transition energies of molecules for the three spectrums (1eV; 0,1eV; 0,01eV) confirmed relative independence of these movements. Franck-Condon's principle is based on independence of timescales that correspond to the movement of electrons and nuclei.

#### INTERACTION OF PHOTONS WITH MOLECULES

Rays of photons of intensity  $I_0$  that hits molecular gas target can be refracted, absorbed or may pass without any interaction. If to these processes correspond intensities:  $I_R$ ,  $I_A$ ,  $I_T$ . It is obvious that:

$$I_R/I_0 + I_A/I_0 + I_T/I_0 = 1. \quad (3)$$

Quotients  $R = I_R/I_0$ ,  $A = I_A/I_0$ ,  $T = I_T/I_0$  are named as coefficients of refraction, absorption and transmission, respectively.

In case of absorption, due to convenient measuring and representation extinction is defined as:

$$E = -\log T \approx -\log(1 - A). \quad (4)$$

By measuring extinction we obtain curves with maximum at places with maximum of absorption. Positions of absorption maximum enable identification of molecular states. Borders of Franck-Condon's region are determined by points in which square of wave function amplitude (probability density)  $|\psi_0|^2$  of ground states of Linear Harmonic Oscillator fall at  $1/e$  of maximum value, and these are so called recurrent points at axis of  $R$ .

#### EXPERIMENTAL SET-UP AND MEASURING PROCEDURES

Measurement of extinction is done with Spekol device whose scheme is shown in Figure 1. Beam of light from the lamp with red-hot metal thread (continuous spectrum) is collimated and reflected by the mirror to a diffraction grate by turning diffraction grate to different parts of the spectrum directed to the gap towards cuvette with test gas ( $\text{Br}_2$  steam), i.e. the decomposition of wavelengths and excitation of  $\text{Br}_2$  molecules is performed. After interaction with the target, the transmitted light is detected by photocell. The intensity of transmitted light for a given wavelength is normalized to the cuvette filled with air. This normalization is needed because of the non-uniform spectral distribution of light sources and because of the non-uniform spectral characteristics (quantum efficiency) of given photocell. For given wavelength of incident light, beam is first passed through an empty cuvette thus determine  $I_0$ , then the procedure is repeated with cuvette in which is the tested gas  $\text{Br}_2$ . Decreasing of intensity of transmitted light (transmission) is measured as the difference of signal from the photocell and worked out with micro-processor for a given wavelength on display as extinction.

Extinction is measured for different wavelengths. The measurement is made on the basis of Franck-Condon's principle, under which a transition to a more excited state is done without changing  $R$ . The goal of experiment is to determine curves of electron energy in excited electronic states of molecules  $\text{Br}_2$  as functions of  $R$  using the Franck-Condon's principle.

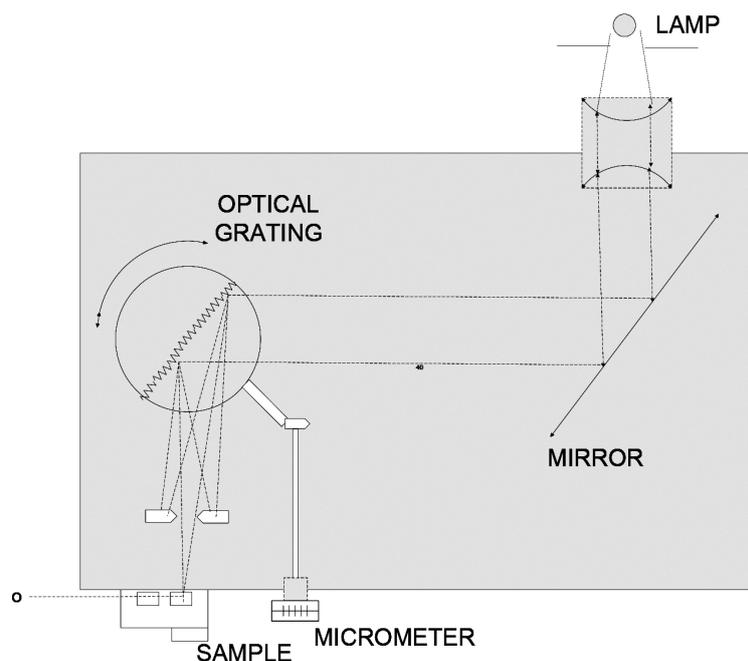


FIGURE 1. Scheme of measuring device

## RESULTS AND DISCUSSION

Software Origin is used in analysis of measured data. The following universal constants are used:

$$e = 1,60 \times 10^{-19} \text{C}, h = 6,63 \times 10^{-34} \text{Js}, \\ c = 2,99 \times 10^8 \text{m/s}.$$

Spectroscopic constants of the ground state  $^1\Sigma_g^+$  of  $\text{Br}_2$  are in agreement with the experimental results (Huber et al. 1979). The following quantities are provided for ground state  $^1\Sigma_g^+$  of molecule  $\text{Br}^{79}\text{Br}^{81}$ :  $\omega_e$  (vibrational constant),  $\omega_e x_e$  (vibrational constant),  $D_e$  (rotational constant),  $B_e$  (rotational constant),  $\alpha_e$  (rotational constant) and  $r_e$  (internuclear distance). The values of these constants are:

$$\omega_e = 323,3 \text{ cm}^{-1}, \omega_e x_e = 1,07 \text{ cm}^{-1}, D_e = 1,971 \text{ eV}, \\ B_e = 0,08091 \text{ cm}^{-1}, \sigma_e = 0,00027 \text{ cm}^{-1} \\ \text{and } r_e = 2,283 \text{ \AA}.$$

According to these data, the Morse function is:  $E(R) = 1,971 \times ((1 - \exp(-1971 \times (R - 2283)))^2 - 1)$  Probability amplitude for the ground state is proportional to:  $\exp(-382 \times (x - 2283))$ .

The values of extinction were measured for the wavelengths of 370 – 570 nm. For the purposes of this research, we performed measurements of extinction for each  $\lambda$  three times, in order to obtain more reliable results. Energy values are calculated as  $E_n[\text{eV}] = hc/\lambda$ , for each  $\lambda$ . The values of extinction are averaged, the absolute error is estimated and the relative error is calculated. The relative error did not exceed 1%. The results are presented in Table 1 and a graph of energy dependence on extinction is drawn (Figure 2).

TABLE 1. Value of extinction for given wavelength

$\lambda$ [nm]	$E_n$ [eV]	E	$\Delta E$
370	3,34	0,136	0,001
380	3,25	0,435	0,004
390	3,17	0,904	0,009
400	3,09	1,304	0,013
410	3,01	1,638	0,025
420	2,94	1,762	0,022
430	2,87	1,724	0,024
440	2,81	1,620	0,015
450	2,75	1,429	0,003
460	2,69	1,301	0,014
470	2,63	1,218	0,024
480	2,57	1,189	0,012
490	2,52	1,074	0,011
500	2,47	0,964	0,008
510	2,42	0,866	0,008
520	2,38	0,671	0,006
530	2,33	0,561	0,005
540	2,29	0,389	0,003
550	2,25	0,314	0,003
560	2,21	0,201	0,002
570	2,17	0,130	0,001

On the graph (Figure 2), are recognized two Gausses slopes and their separation (deconvolution) is done. The complete Gausses functions are determined and calculations are presented for the first (Table 2) and second (Table 3) Gausses slope, respectively. The maximum of the first Gausses slope is 0,962 and for the second is 1,598.

Method of mirror symmetry is applied on Gausses slopes of extinction and symmetrical extinction values ( $E_s$ ) are got. The results are presented in Tables 2 and 3. From

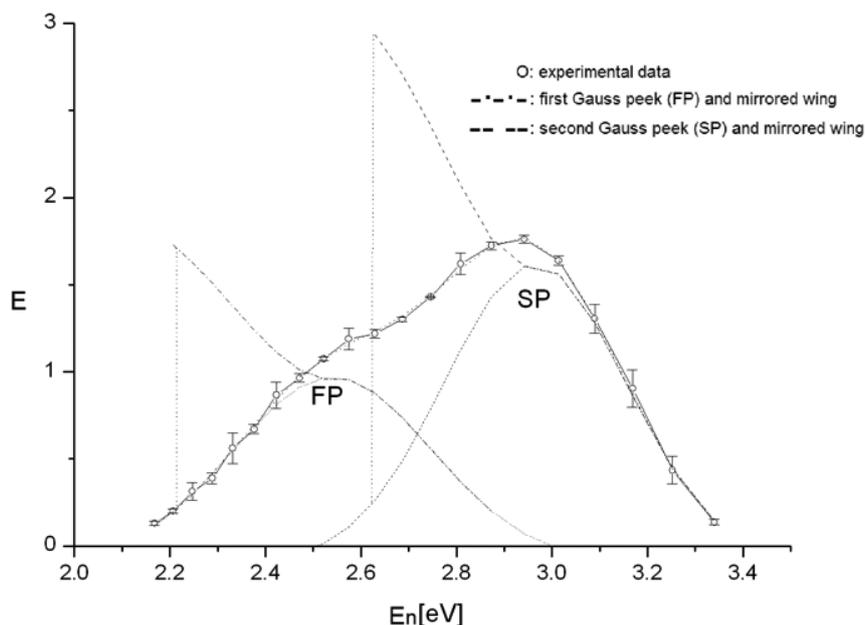


FIGURE 2. Graph of energy dependence on extinction

TABLE 2. Coordinates of the first Gauss function and symmetrical extinction values

En[eV]	E	Es	R[Å]
2,17	-	-	-
2,21	0,198	1,726	2,342
2,25	0,297	1,627	2,335
2,29	0,415	1,509	2,326
2,33	0,547	1,377	2,316
2,38	0,684	1,240	2,305
2,42	0,812	1,112	2,296
2,47	0,913	1,011	2,288
2,52	0,966	0,958	2,284
2,57	0,956	0,956	2,284
2,63	0,877	0,877	2,278
2,69	0,737	0,737	2,268
2,75	0,558	0,558	2,254
2,81	0,368	0,368	2,240
2,87	0,199	0,199	2,227
2,94	-	-	-
3,01	-	-	-
3,09	-	-	-
3,17	-	-	-
3,25	-	-	-
3,34	-	-	-

TABLE 3. The coordinates of the second Gauss function and symmetrical extinction values

En[eV]	E	Es	R[Å]
2,17	-	-	-
2,21	-	-	-
2,25	-	-	-
2,29	-	-	-
2,33	-	-	-
2,38	-	-	-
2,42	-	-	-
2,47	-	-	-
2,52	-	-	-
2,57	-	-	-
2,63	0,262	2,934	2,342
2,69	0,487	2,709	2,333
2,75	0,785	2,411	2,320
2,81	1,125	2,071	2,306
2,87	1,433	1,763	2,294
2,94	1,607	1,607	2,287
3,01	1,561	1,561	2,285
3,09	1,283	1,283	2,274
3,17	0,863	0,863	2,257
3,25	0,445	0,445	2,239
3,34	0,144	0,144	2,227

ground state of Linear Harmonic Oscillator (LHO) borders of Franck-Condon's region are got:  $2,227 \times 10^{-10} \text{m}$  -  $2,342 \times 10^{-10} \text{m}$ .

Tables of dependence among R and the excitation energy are given (Tables 2 & 3). On the basis of these tables are determined potential curves of excited states of molecules in the Franck-Condon's area (Figure 2). Curves of energy excitations are also given separately (Figure 3).

The potential curves of excited states are put in the same graph with the Morse curve of the ground state. The following graph is got (Figure 4), where the curves of two excited states are seen as well as the recurrent points.

#### DISCUSSION AND CONCLUSION

The method of gas spectroscopy is applied for direct measuring of extinction of  $\text{Br}_2$  molecules. Graph of energy dependence

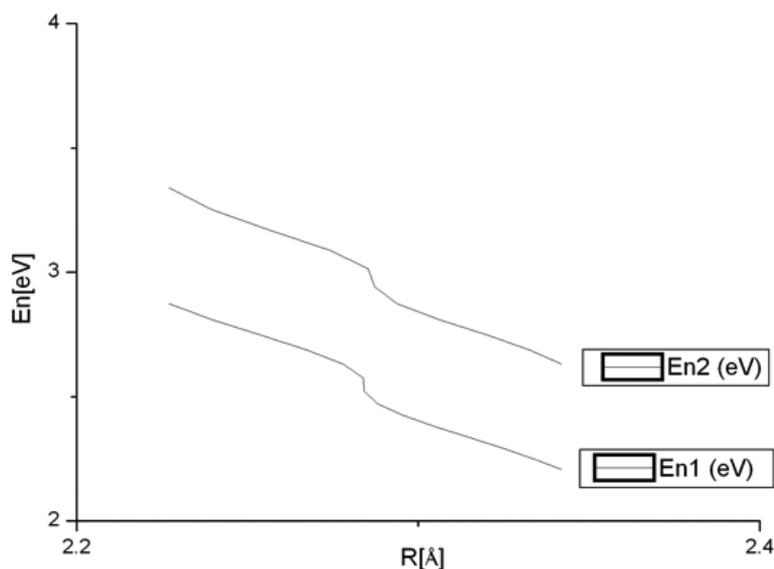


FIGURE 3. Potential curves of excited states of molecules in the Franck-Condon's area

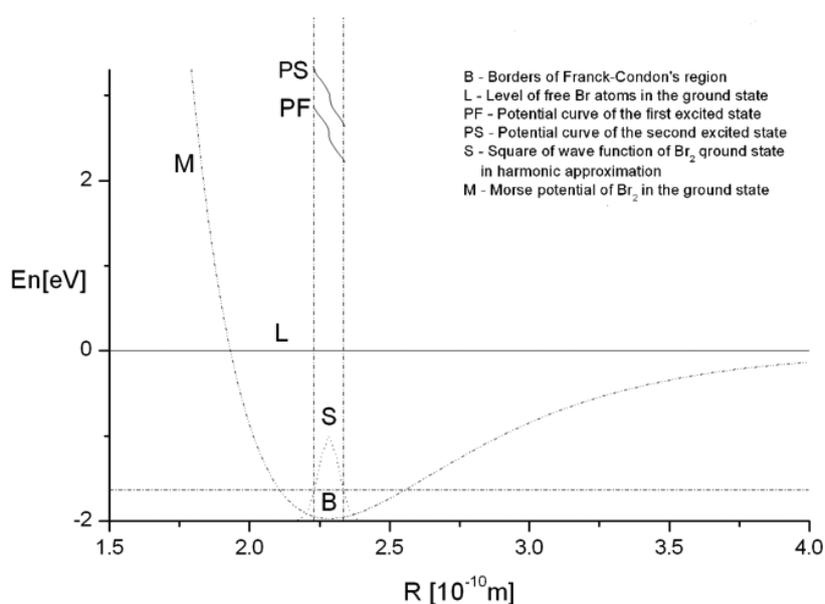


FIGURE 4. Morse curve of the ground state of  $\text{Br}_2$

on extinction is drawn and analyzed by computer software Origin. Graph structure is recognized as linear combination of two Gausses slopes. Further analysis enabled determination of Franck Condon's borders. On those bases, the potential energy curves of diatomic molecules  $\text{Br}_2$  are estimated and drawn. In further research this method will be applied on measuring devices with higher sensitivity that could result in determination of finer structures of potential curves.

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