

## **Iodine molecule covalente excited states as determined by threshold electron spectrometry\***

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The iodine molecule has been investigated by a threshold electron spectrometer in the incident electron energy range from 1.00 eV to 3.5 eV. From the threshold electron spectrum contributions for excitation of three states known from optical spectrometry have been subtracted. The remaining signal has been interpreted by four curves similar in shape to those in absorption optical spectroscopy into antibonding energy states. The detected maxima have been attributed to the following valence excited states of the iodine molecule:  $^3\Pi_{2u}(2_u)$ ,  $^3\Pi_{0u}(0_u)$ ,  $^3\Pi_{2g}(2_g)$ , and  $^3\Pi_{1g}(1_g)$ , respectively. With the knowledge of the energy ranges within which the signal from a particular state appears, the predicted values of equilibrium distances of iodine atom nuclei and estimated values of vibrational transition frequency potential energy curves have been constructed, too.

**Keywords:** electron impact, iodine molecule, excitation, valence states.

### INTRODUCTION

There is a great number of papers devoted to the investigation of the iodine molecule. In most of them either absorption or emission spectroscopy was applied to determine the energy location of rotationally, vibrationally and electronically excited states. The results of these studies are reviewed by Mulliken,<sup>1</sup> Herzberg,<sup>2</sup> Mulliken,<sup>3</sup> Coxon,<sup>4</sup> Mizushima<sup>5</sup> and Huber and Herzberg.<sup>6</sup> Optical spectroscopy methods have an extremely high energy resolution, which enables the detection of a great number of excited states. However, these traditional optical methods cannot be used for the detection of optically forbidden transitions, due to selection rules.

Energetically narrow electron beams are inferior to optical methods in terms of energy resolution. The advantage of electron-molecule collision experiments is that the conservation of angular momentum introduces different conditions than in the photon-molecule interaction. In these experiments excitation of states, the

\* Dedicated to Professor Slobodan Ribnikar on the occasion of his 70th birthday.

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transition from the molecular ground state to which is optically forbidden, can be detected. The iodine molecule has been approached by the methods of high resolution electron spectroscopy in a small number of experiments. Here some results of an the attempt to understand the excitation of the iodine molecule by incident electrons are presented. Some preliminary results have been already reported by Jureta *et al.*<sup>7</sup>

#### IODINE MOLECULE COVALENT EXCITED STATES

Two iodine atoms in the ground  $2P_{3/2}$  state and/or in the spin excited  $2P_{1/2}$  state with  $5p^5$  outermost electrons give in the LCAO MO treatment altogether fourteen molecular orbitals. The  $(5\sigma_g)^2 (5\pi_u)^4 (5\pi_g)^4 (5\sigma_u)^0$ , abbreviated as 2440, arrangement of the ten valence shell electrons is the molecular ground state  $X^1\Sigma_{0+g}(0^+_g)$ .

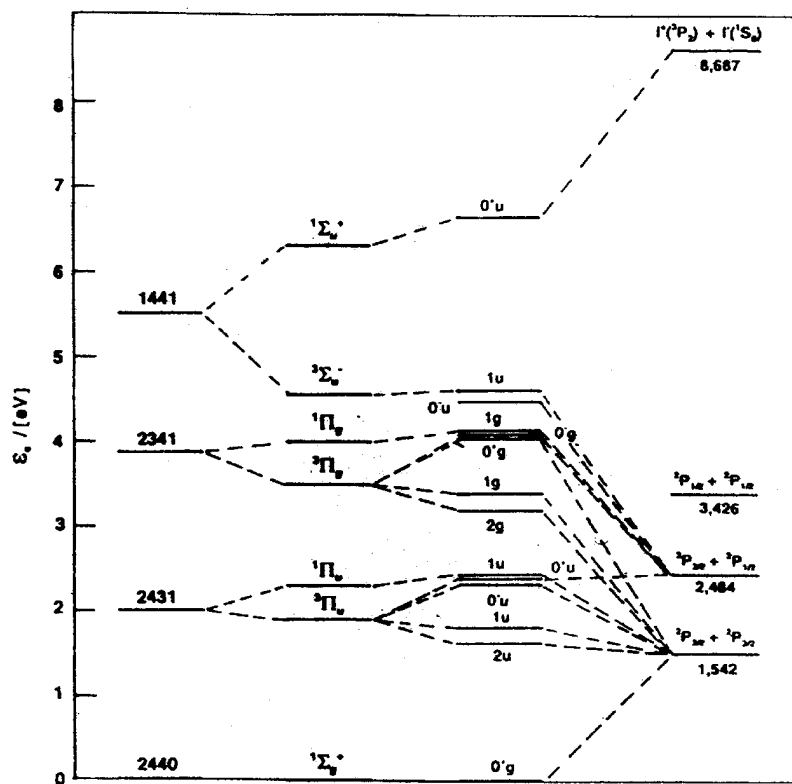


Fig. 1. Schematic correlation diagram for the low-lying iodine molecule valence-shell states with their dissociative products (Mullikan<sup>1</sup>).

Single electron transitions between the valence shells lead to electronic states lowest in energy. They are formed by the promotion of an electron from a filled orbital to the vacant  $(5\sigma_u)$  one. Fig. 1. shows schematically the lowest energy configurations obtained in this way, with both Hund's case (a) and (c) notations. In

the later case only  $\Omega$  (the electronic angular momentum along the internuclear axis) is defined and the splitting of 0 states into  $0^+$  and  $0^-$ , and  $^3\Sigma^{+(-)}$  into 1 and  $0^{+(-)}$  components denoted. In an important paper, Mulliken<sup>3</sup> predicted atomic species that are to be expected as dissociation products for each of the valence shell states, implying the non crossing rule, according to which states of the same  $\Omega$  value and same parity cannot cross.

In the latest review of diatomic molecule state parameters Coxon,<sup>4</sup> Mizushima<sup>5</sup> and Huber and Herzberg<sup>6</sup> listed reliable data only for the following three valence electronic states of the iodine molecule:

$$X\ ^1\Sigma_{0+g}(0^+_g); A\ ^3\Pi_{1u}(1_u); \text{ and } B\ ^3\Pi_{0+u}(0^+_u);$$

of all the possible states, while only a guess is given for the  $A'\ ^3\Pi_{2u}(2_u)$  state.

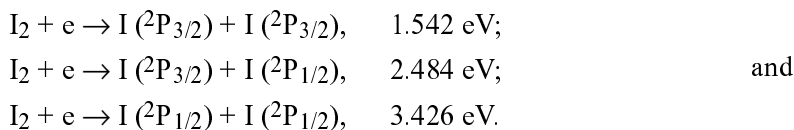
### EXPERIMENTAL

The threshold spectrometer used for this study is similar to those described by Cvejanović and Read<sup>8</sup> and Cvejanović *et al.*<sup>9</sup> The spectrometer consists of two functional parts: a source of electrons, which are scattered at the iodine molecule gas beam at right angles to the gas beam direction, and a threshold electron analyzer. The hemispherical monochromator produces a well collimated electron beam with an energy half width (FWHM) of 25 meV. The scattered electrons, whose energy falls within the analyzer's acceptance window of 0 - 10 meV, are extracted with a high efficiency from the target region through an opening in the surrounding mesh shield. The threshold electrons are separated from those of higher energy, traveling in the same direction, by the use of a small cylindrical mirror analyzer, and are individually detected by a channel electron multiplier.

The energy calibration of the threshold spectrum was obtained by mixing iodine with xenon, the first two excited states  $6s'$  ( $J = 2.1$ ), at 8.315 eV and 8.437 eV respectively, of which are conveniently situated close to the sharp structures in the threshold spectrum. The accuracy of the energy scale is within 0.01 eV (one channel width).

### IODINE MOLECULE THRESHOLD ELECTRON SPECTRUM

The threshold spectrum of valence states, for incident electron energies between 1.0 eV and 3.5 eV is shown in Fig. 2, with marked dissociation limits for following processes:



The lowest dissociation energy of 1.542 eV was obtained by Le Roy.<sup>10</sup> The energy differences for the higher dissociation limits are due to spin excitation of the iodine atom from the  $^2\text{P}_{3/2}$  to the  $^2\text{P}_{1/2}$  state, which is equal to 0.942 eV, according to Moore.<sup>11</sup>

In analyzing the measured threshold spectrum we started from data available for transitions to optically allowed states and a review of Coxon.<sup>4</sup> The most thoroughly investigated absorption spectrum was published by Tellinghuisen<sup>11</sup> and

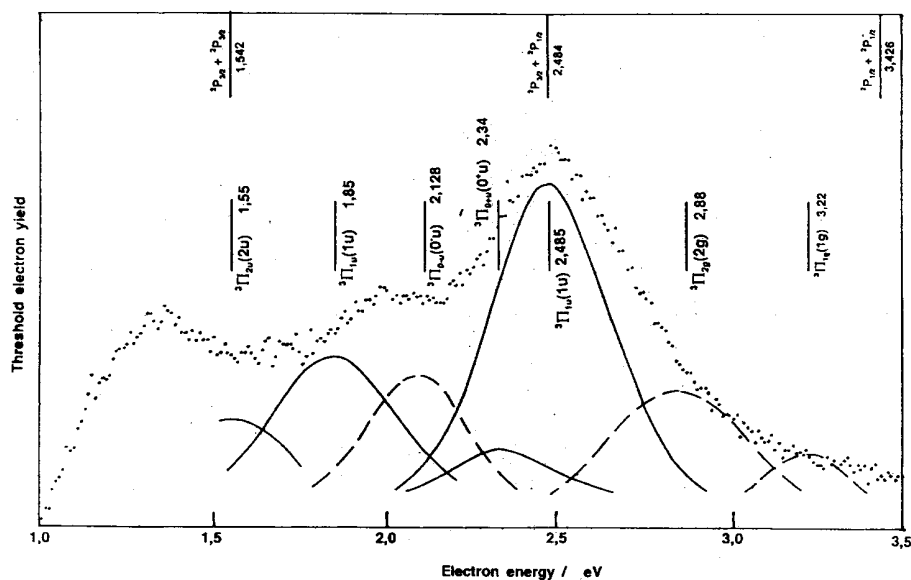


Fig. 2. Threshold electron spectrum of the iodine molecule.

it was interpreted as being due to transitions to three electronic states:  $^3\Pi_{1u}(1_u)$ ,  $^3\Pi_{0+u}(0^+_u)$  and  $^1\Pi_{1u}(1_u)$ , corresponding to the maxima of the absorption curves at 1.850 eV; 2.340 eV and 2.485 eV, respectively. Excitation of these three states contribute to the measured threshold electron spectrum. Thus, the absorption curves of Tellinghuisen<sup>12</sup> were normalized to the threshold spectrum so as to fit them as well as possible in the energy ranges around 1.85 eV and 2.48 eV, where maxima are distinguishable.

It is obvious that transitions to some other states, apart of these three known from optical absorption measurements, contribute to the threshold spectrum. The net signal due to excitation of these other states was obtained by subtracting the contributions from the transitions to  $^3\Pi_{1u}(1_u)$ ,  $^3\Pi_{0+u}(0^+_u)$  and  $^1\Pi_{1u}(1_u)$  states from the measured spectrum. The remaining signal could be approximated quite well by three gaussian shaped curves with maxima at 1.56 eV; 2.12 eV and 2.88 eV.

Mulliken<sup>3</sup> analyzed the iodine molecule and gave expected values for vertical excitation of electronic states dissociating to neutral iodine atoms. These values are presented in Table I. According to it, in the energy range below the  $^3\Pi_{1u}(1_u)$  state, only the  $^3\Pi_{2u}(2_u)$  electronic state could be located, and so the continuum-like spectrum with a maximum at 1.56 eV can be attributed to excitation of this state. Between the  $^3\Pi_{1u}(1_u)$  and  $^3\Pi_{0+u}(0^+_u)$  states, contributions from the transition to the  $^3\Pi_{0-u}(0_u)$  state is possible, which led us to the suggestion that the maximum at 2.12 eV is due to transition to this electronic state.

The threshold electron spectrum at energies higher than 2.50 eV could come from transitions to some repulsive electronic states. Le Roy<sup>10</sup> suggested that the

state  ${}^3\Pi_{0-u}(0_u^-)$  could have an extremely small barrier of  $13.1 \pm 1.3 \text{ cm}^{-1}$  (0.0016 eV), dissociating to two ground state iodine atoms, at the 1.542 eV limit. The other two candidates for contributing to the threshold spectrum are  ${}^3\Pi_{2g}(2_g)$ , and  ${}^3\Pi_{1g}(1_g)$ , with vertical excitation energies predicted by Mulliken<sup>3</sup> of 3.2 eV and 3.4 eV, respectively. We are inclined to suggest that the signal with the maximum at 2.88 eV is due to transition to the  ${}^3\Pi_{2g}(2_g)$  state, while the threshold electron signal around 3.20 eV could come from transition to the  ${}^3\Pi_{1g}(1_g)$  state.

The threshold electron signal below 1.542 eV, the lowest dissociation limit, could be partly instrumental in origin, or could come from excitation of the  ${}^3\Pi_{2u}(2_u)$  state vibrational levels and/or of some high vibrational levels of the  ${}^1\Sigma_g^+(0_g^+)$  ground state *via* resonant electron attachment processes with the formation of short lived excited negative molecular ions  $I_2^{*-}$  of configuration  ${}^2\Pi_{g,3/2}$  and  ${}^2\Pi_{g,1/2}$  (Kurepa<sup>13</sup>).

#### IODINE VALENCE EXCITED STATE POTENTIAL ENERGY CURVES

The potential energy curves of the low-lying electronic states are presented in Fig. 3. The curve for the  ${}^1\Sigma_g^+(0_g^+)$  ground state was derived by Coxon,<sup>14</sup> from an analysis of absorption spectra, and a part of the curve of the excited  ${}^3\Pi_{0+u}(0_u^+)$  state by Tellinghuisen.<sup>12</sup> The other curves were obtained by using the Morse equation with state parameters taken from review papers or proposed by recent investigations (see Table I).

TABLE I. Valence orbital excited states

Orbitals		a	a	b	c	Vertical Excitation in eV			State Parameters			
		+	+	+	+							
		a	b	b	d	Mulliken	Exp.	$T_e/\text{eV}$	$\omega_e/\text{cm}^{-1}$	$r_e/10^{-10}$ m		
2440	$^1\Sigma_g^+$	0 <sup>+</sup>	+	−	−	−		0	214.5	2.666	X	
		2	+	−	−	−	1.673	<b>1.56</b>	0.942	106.29	<b>3.09</b>	A'
2431	$^3\Pi_u$	1	+	−	−	−	1.79	1.85	1.352	96.2	<b>3.02</b>	A
		0 <sup>−</sup>	+	−	−	−	2.33	<b>2.12</b>	1.502	50	<b>3.10</b>	B'
		0 <sup>+</sup>	−	+	−	−	2.355	2.340	1.955	125.69	3.024	B
2431	$^1\Pi_u$	1	+	−	−	−	2.516	2.485	−	repulsive	−	B''
		2	+	−	−	−	3.2	<b>2.88</b>	−	−	−	−
2341	$^3\Pi_g$	1	+	−	−	−	3.4	<b>3.20</b>	−	−	−	−
		0 <sup>−</sup>	−	+	−	−	4.1	−	−	−	−	−
		0 <sup>+</sup>	+	−	−	−	4.1	−	−	−	−	−
2341	$^1\Pi_g$	1	−	+	−	−	4.1	−	−	−	−	−
	$^3\Sigma_u^+$	0 <sup>−</sup>	+	−	−	−	4.5	−	−	−	−	−
1441		1	−	+	−	−	4.57	−	−	−	−	−
	$^1\Sigma_u^+$	0 <sup>+</sup>	−	−	−	+	6.77	−	5.134	104.41	3.45	D

Abbreviations: a - I ( ${}^2P_{3/2}$ ); b - I ( ${}^2P_{1/2}$ ); c - I<sup>+</sup> ( ${}^3P_2$ ); d - I<sup>–</sup> ( ${}^1S_0$ ). State parameters determined from the present experiments are given in bold characters.

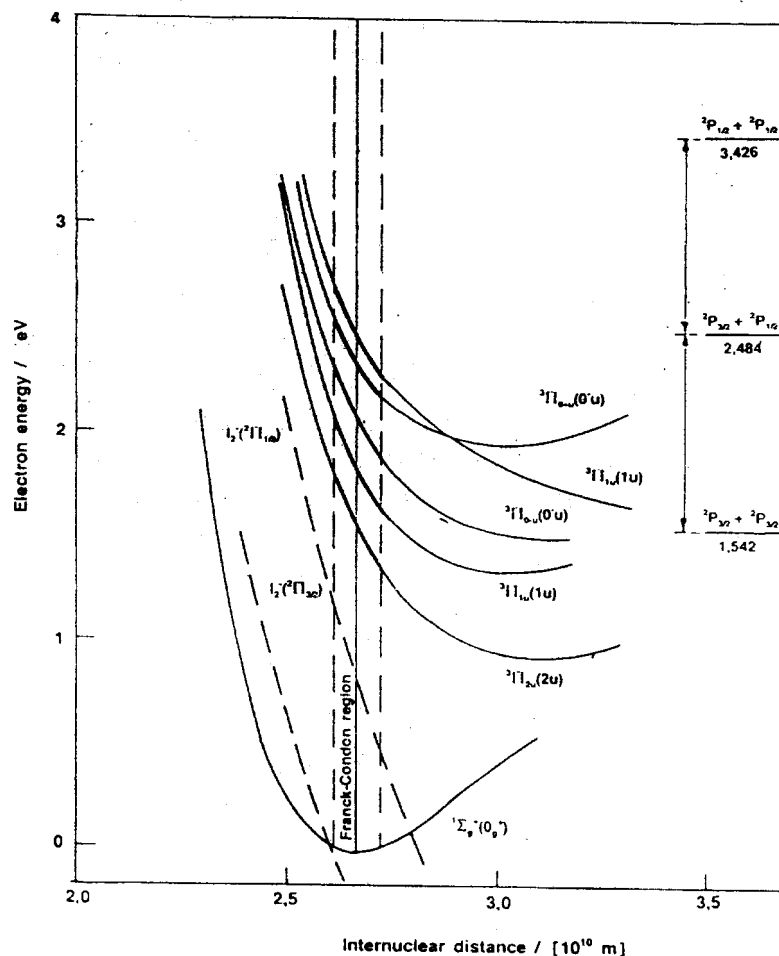


Fig. 3. The potential energy curves of ground state and covalent valence states of the iodine molecule.

Only approximate values of the state parameters for the  $^3\Pi_{2u}(2_u)$  state are given by Huber and Herzberg.<sup>6</sup> The  $T_e$  value suggested by Mulliken,<sup>3</sup> on the basis of the analysis of Tellinghuisen,<sup>12</sup> was  $10100\text{ cm}^{-1}$  (1.252 eV). Kawasaki *et al.*<sup>15</sup> have recently investigated the excitation of the  $\text{I}_2$  molecule by multiple photon absorption. They agreed, following the conclusions of Tellinghuisen,<sup>12</sup> that part of the fluorescence spectrum could be interpreted as a transition from the upper  $^3\Pi_{2g}(2_g)$  state, of structure 1432, to the lower  $^3\Pi_{2u}(2_u)$  state, and that the minimum of the lower state potential energy curve should be  $7600\text{ cm}^{-1}$  (0.942 eV). This would then give a value for the dissociation energy of  $D_e = 0.614\text{ eV}$ . With  $\omega_e = 106.29\text{ cm}^{-1}$ , as suggested by Tellinghuisen,<sup>16</sup> we calculated the Morse curve for the  $^3\Pi_{2u}(2_u)$  state, and positioned it in the diagram so that it crosses the ground state

$r_e$  distance at an energy of 1.56 eV, the value corresponding to the maximum of the threshold electron signal. With this fit, an equilibrium distance of  $r_e = 3.09 \times 10^{-10}$  m was obtained for the  $^3\Pi_{2u}(2_u)$  state.

The approximate values of the parameters for the  $^3\Pi_{1u}(1_u)$  state, given by Huber and Herzberg,<sup>6</sup> are:  $T_e = 11888 \text{ cm}^{-1}$  (1.473 eV) and  $\omega_e = 44.0 \text{ cm}^{-1}$  and no value for  $r_e$ . In interpreting the fluorescence spectra by multiphoton absorption of  $I_2$  Kawasaki *et al.*<sup>15</sup> suggested a slightly different value for the position of the potential curve minimum of  $T_e = 11790 \text{ cm}^{-1}$  (1.468 eV). Recent measurements of Pigache *et al.*,<sup>17</sup> by excitation energy transfer, led to:  $T_e = 10906 \text{ cm}^{-1}$  (1.352 eV) and  $\omega_e = 96.2 \text{ cm}^{-1}$ . The calculated dissociation energy of  $D_e = 0.203 \text{ eV}$  is in accordance with the corresponding value of Gestenkorn *et al.*<sup>18</sup> With these state parameters, we calculated the Morse curve and located it in the diagram in Fig. 3. so as to cross the ground state equilibrium distance at an energy of 1.85 eV, in accordance to the absorption maximum of Tellinghuisen.<sup>12</sup> The best fit was obtained for  $r_e = 3.02 \times 10^{-10}$  m, which is lower than the value predicted by Tellinghuisen.<sup>12</sup>

Huber and Herzberg<sup>6</sup> suggested that the  $^3\Pi_{0-u}(0_u^-)$  state is repulsive, although Mulliken<sup>3</sup> gives a negative slope to the potential energy curve at larger internuclear distances, leading to a potential minimum. We have calculated the Morse curve for this state taking that the potential curve minimum is 0.040 eV, and  $\omega_e \cong 50 \text{ cm}^{-1}$ . The resulting curve was also positioned in the diagram in Fig. 3, so as to cross the value of the ground state  $r_e$  distance at 2.12 eV, the value of the gaussian curve maximum with which the threshold spectrum was interpreted in this energy range. The best fit was obtained for  $r_e = 3.10 \times 10^{-10}$  m, for the  $^3\Pi_{0-u}(0_u^-)$  state. The so generated potential energy curve corroborates the analysis of Mulliken,<sup>3</sup> and his conclusion that it can not cross the curve of the  $^3\Pi_{0+u}(0_u^+)$  state for small internuclear distances.

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### ИЗВОД

#### КОВАЛЕНТНА ПОБУЂЕНА СТАЊА МОЛЕКУЛА ЈОДА ОДРЕЂЕНА ЕЛЕКТРОНСКОМ СПЕКТРОМЕТРИЈОМ ПРАГОВА

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Молекул јода је испитиван помоћу електронског спектрометра прагова у области енергије упадних електрона од 1,00 eV до 3,5 eV. Од спектра прагова одузет је сигнал који припада побуђивању трију стања познатих из оптичке спектрометрије. Преостали сигнал интерпретиран је помоћу четири криве облика сличног онима из апсорпционе

оптичке спектрометрије за прелаз у развезујуће енергијско стање. Детектовани максимуми приписани су побуђењу следећих валентно побуђених стања молекула јода:  $^3P_{2u}(2u)$ ,  $^3P_{0u}(0u^-)$ ,  $^3P_{2g}(2g)$  и  $^3P_{1g}(1g)$ . Уз познавање домена енергија у којима се појављује сигнал за побуђење одређеног стања, предвиђених вредности равнотежних растојања језгара атома јода и процењених вредности учестаности за вибрационо побуђивање, конструисане су криве потенцијалних енергија за та стања.

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