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Analysis of the long range potential of iodine in the B $^3\Pi^+_{ou}$ state

S. Gerstenkorn, P. Luc

Laboratoire Aimé Cotton (*), C.N.R.S. II, Bâtiment 505, 91405 Orsay Cedex, France

and C. Amiot

Laboratoire de Physique Moléculaire et d'Optique Atmosphérique (*),
C.N.R.S., Bâtiment 221, Campus d'Orsay, 91405 Orsay Cedex, France

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Résumé. — Le potentiel quantique de l'état B $^3\Pi^+_{ou}$ de l'iode, s'étendant depuis le niveau fondamental $v = 0$ jusqu'au niveau $v = 80$ (soit 99,96 % du puits de potentiel), a été déterminé à l'aide d'une méthode variationnelle (IPA). L'analyse de la branche externe de ce potentiel fait appel au développement multipolaire de l'énergie d'interaction limité au terme C_{10}/R_v^{10}; l'énergie d'échange $V_{ex}(R)$ et les effets hyperfins étant négligés. Dans la région analysée (entre 7 et 12 Å), l'énergie d'échange $V_{ex}(R)$ estimée est faible et pourrait même être contrebalancée par la contribution du terme C_{12}/R_v^{12} ; de plus, l'énergie de la limite de dissociation D_e ainsi que les valeurs des coefficients C_n sont pratiquement insensibles au nombre de points tournants considérés. Les valeurs de D_e et de C_n sont trouvées respectivement égales à :

$$\begin{aligned} D_e &= 4\,381{,}249_2 \pm 0{,}001\ \mathrm{cm}^{-1} \\ C_5 &= 3{,}161(33) \times 10^5\ \mathrm{cm}^{-1}\,\text{Å}^5 \\ C_6 &= 1{,}506(43) \times 10^6\ \mathrm{cm}^{-1}\,\text{Å}^6 \\ C_8 &= 0{,}248(14) \times 10^8\ \mathrm{cm}^{-1}\,\text{Å}^8 \\ C_{10} &\leqslant 0{,}042(3) \times 10^{10}\ \mathrm{cm}^{-1}\,\text{Å}^{10}, \end{aligned}$$

où les incertitudes sont celles correspondant uniquement aux erreurs d'ajustement obtenues à partir des points tournants calculés par la méthode IPA.

Abstract. — A quantum mechanical potential energy curve (IPA potential) of the iodine B $^3\Pi^+_{ou}$ state was determined. The analysis of the outer branch of this potential (which encompasses 99.96 % of the depth well from $v = 0$ to $v = 80$) was carried out by means of the multipole expansion of the interaction energies truncated up to the C_{10}/R_v^{10} term; the exchange energies $V_{ex}(R)$ being neglected and hyperfine effects ignored. In the analysed region (from 7 to 12 Å) the estimated $V_{ex}(R)$ are small and may even be cancelled by the contribution of the neglected term C_{12}/R_v^{12}; moreover, the dissociation limit energy D_e and the C_n coefficients are not depending of the number of turning points considered. The values of D_e and C_n are respectively found to be equal to :

$$\begin{aligned} D_e &= 4\,381.249_2 \pm 0.001\ \mathrm{cm}^{-1} \\ C_5 &= 3.161(33) \times 10^5\ \mathrm{cm}^{-1}\,\text{Å}^5 \\ C_6 &= 1.506(43) \times 10^6\ \mathrm{cm}^{-1}\,\text{Å}^6 \\ C_8 &= 0.248(14) \times 10^8\ \mathrm{cm}^{-1}\,\text{Å}^8 \\ C_{10} &\leqslant 0.042(3) \times 10^{10}\ \mathrm{cm}^{-1}\,\text{Å}^{10}, \end{aligned}$$

the quoted uncertainties being those resulting from fits using the calculated IPA potential.

(*) Laboratoires associés à l'Université Paris-Sud.

1. Introduction.

Several analysis of the RKR [1] long range potential of the B $^3\Pi_{ou}^+$ state of iodine were made in the past [2-4]. In this paper an improved potential energy of the B state is determined using the « inverted perturbation approach » (IPA) method [5, 6]. This method, which gives a quantum mechanical potential curve free of the approximations generally associated with the RKR method, has been already used with success in the study of several diatomic molecules such as Mg_2 [7], Ca_2 [8], Li_2 [9], LiH [10], Cs_2 [11] and CO [12]. The IPA method is based on an optimization procedure of the rotationless potential $V_0(R)$, where the RKR potential computed from the Dunham coefficients and expansion coefficients of the centrifugal distortion constants (CDC) serve as starting point of the variational method. Throughout this work we have used Vidal's IPA computer program kindly supplied to us [13]. Details about the IPA method can be found in the different papers of references [5-12]. We just recall that, having determined the quantum mechanical potential $V_0(R)$, it is then possible to calculate the vibrational $G(v)$ quantities given as the eigenvalues :

$$G(v) = E_{v,J=0}$$

and the rotational constants $\langle B(v) \rangle$ which are the expectation values of $1/R^2$:

$$\langle B(v) \rangle = [h/(4\pi\mu c)] \langle \Psi_{v,J=0} | 1/R^2 | \Psi_{v,J=0} \rangle .$$

The IPA potential of the B state up to the $v = 80$ level, located only 1.64 cm^{-1} from the dissociation limit, is given in section 2. Section 3 contains the results of the analysis of the B $^3\Pi_{ou}^+$ state long range potential, i.e. the dissociation limit energy D_e and the long range C_n coefficients. It is followed by the discussion of the validity of the results obtained according to different assumed approximations. Finally, a comparison is made with theoretical values of the C_5 and C_6 long range coefficients [14-17].

2. The IPA potential of the B state.

It is well known that, in the analysis of the B ← X transition, the vibrational and rotational constants (and to certain amount the CDC also) of both X and B states are strongly correlated. To be coherent, it was wise to construct first the IPA potential of the X state, limited to $v'' = 19$, the last level observed in absorption. Then, using the IPA potential of the X state (and the corresponding CDC computed from this IPA potential), a least squares fit was performed with the 17 800 wavenumbers corresponding to the data field given on figure 1, the method following the iterative procedure described in reference [18]. After two iterations, convergence was achieved and the molecular constants G_v and B_v of the B state were obtained.

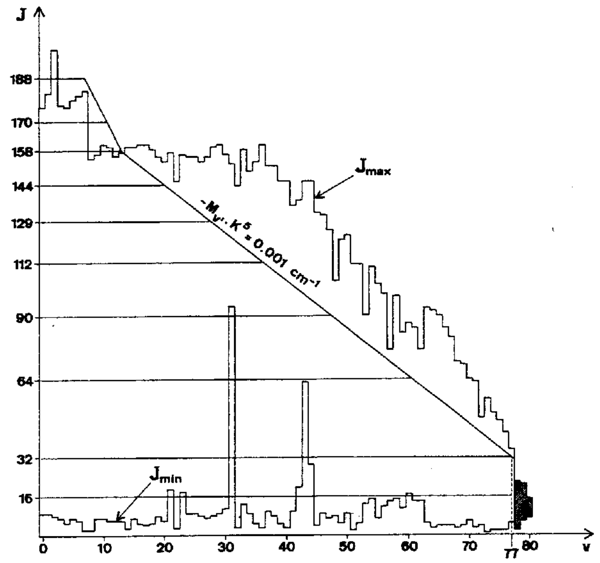

Fig. 1. — Data field and $E_{v,J}$ values that were used in the IPA method for calculating the IPA potential. The data above the full line $-M_v K^5 = 0.001\ cm^{-1}$ and the hachured area were disregarded ($K = J(J+1)$). Lines J_{min} and J_{max} represent the minimum and maximum J values observed for each vibrational level.

The sets of Dunham coefficients describing the G_v and B_v constants and the sets of exponential expansion coefficients representing the computed CDC values (D_v, H_v, L_v and M_v) which were obtained are reproduced in table I. (After the last iteration the root mean square error between the computed wavenumbers (using the coefficients of Table I) and the measured ones was found to be equal to $2.2 \times 10^{-3}\ cm^{-1}$).

These sets of coefficients serve as starting data for computing the IPA potential of the B state.

The vibrational term values $G(v)$, the turning points R_{min} and R_{max} and the expectation $\langle B(v) \rangle$ values of $(1/R^2)$ determined from the IPA potential are listed in table II. The data field sampled by the IPA method was limited to the region beyond the full line $-M_v K^5 = 0.001\ cm^{-1}$, in order to avoid difficulties occurring from neglected higher order centrifugal distortion constants (N_v, O_v ...) as discussed in reference [18]; the hatched region was also disregarded (as shown in Fig. 1) and the J values were chosen according to a $J(J+1)$·progression. More precisely the following data field $J(v_{min} - v_{max})$ define the $E_{v,J}$ values of the selected levels : 16(0-77), 32(0-77), 64(0-59), 90(0-46), 112(0-36), 129(0-27), 144(0-20), 158(0-13), 170(0-11), 182(0-7).

The eigenvalues $G(v)$ of the levels $v = 78$, 79 and 80 are extrapolated values ; in other words, we have not included experimental data deduced from laser induced fluorescence (hatched region Fig. 1) which were known to be less accurate than the Fourier spectroscopy data. However, the extrapolated eigenvalues and the expectation $\langle B(v) \rangle$ values agree well with the experimental ones, a fact already recognized in a recent paper [19].

Table I. — *Expansion coefficients of the* B *state used to calculate the IPA potential.* Y_{i0} *and* Y_{i1} *: Dunham expansion coefficients for vibrational and rotational constants;* $Y_{il}(l = 2, 3, 4$ *and* $5)$ *: exponential expansion coefficients for the centrifugal distortion constants according* $CDC = \exp \sum Y_{il}(v + 1/2)^i$.

Y_{i0}	Y_{i1}	Y^*_{i2}	Y^*_{i3}	Y^*_{i4}	Y^*_{i5}
0.15661940853802D+05	0.29000727108300-01	-.1890242234D+02	-.337189945D+02	-.4730510+02	-.5985D+02
0.12566869517813D+03	-.14943740681 1D-03	0.17571610200-01	0.77704316D-01	0.109274D+00	0.7728D-01
-.75039983603948D+00	-.12603991 6187D-05	0.1469260052D-03	0.10422968D-02	0.456705D-02	0.1745D-01
-.41440414502073D-02	0.36084385240 4D-07	0.4918243008D-04	-.25639673D-03	-.802422D-03	-.1581D-02
0.22489315808648D-03	-.11893676478 4D-07	-.7352761438D-05	0.35991553D-04	0.711468D-04	0.7548D-04
-.32286825302082D-04	0.16083646075 9D-08	0.7322594964D-06	-.28306620D-05	-.355924D-05	-.2032D-05
0.28274026782231D-05	-.14014992157 2D-09	-.4867776634D-07	0.13695909D-06	0.106988D-06	0.3105D-07
-.16976059525912D-06	0.81708227314 6D-11	0.2233046290D-08	-.42618198D-08	-.197188D-08	-.2500D-09
0.72483391984314D-08	-.32952610102 1D-12	-.7204734178D-10	0.86705863D-10	0.218611D-10	0.8254D-12
-.22366834361621D-09	0.93725931617 6D-14	0.1641868691D-11	-.11452403D-11	-.133995D-12	
0.50241595329130D-11	-.18928106706 1D-15	-.2624266807D-13	0.94600774D-14	0.349444D-15	
-.81831500764874D-13	0.26987522892 1D-17	0.2878337216D-15	-.44418160D-16		
0.95205749185164D-15	-.26572340935 5D-19	-.2064826062D-17	0.90585760D-19		
-.76837892433947D-17	0.17203214351 8D-21	0.8731100972D-20			
0.40758033226391D-19	-.65929044407 8D-24	-.1650469511D-22			
-.12752869307005D-21	0.11334960229 7D-26				
0.17806207411211D-24					

Table II. — *IPA potential : eigenvalues* $G(v)$, *expectation* $\langle B(v) \rangle$ *values,* R_{min} *and* R_{max} *for* $v = 0$ *to* $v = 80$ (B $^3\Pi^+_{0u}$ *state). The uncertainties of the eigenvalues* $G(v)$ *resulting from the whole data field, are estimated to be equal to* 0.4×10^{-3} cm^{-1}, *a value which is five times lower than the standard deviations between the measured and calculated wavenumbers.*

v	G(v)	R_{min}	R_{max}	$10^2\langle B(v)\rangle$	v	G(v)	R_{min}	R_{max}	$10^2\langle B(v)\rangle$
0	62.6189	2.964853	3.095199	2.8925480	41	3681.1672	2.653684	4.373307	1.9438270
1	186.7742	2.923267	3.150219	2.8773660	42	3727.4362	2.651882	4.419551	1.9093280
2	309.3957	2.896318	3.190852	2.8619380	43	3771.7111	2.650174	4.467568	1.8742690
3	430.4636	2.875375	3.225740	2.8462590	44	3814.0191	2.648555	4.517468	1.8386650
4	549.9585	2.857939	3.257390	2.8303190	45	3854.3900	2.647025	4.569366	1.8025300
5	667.8608	2.842873	3.286953	2.8141050	46	3892.8562	2.645578	4.623390	1.7658770
6	784.1505	2.829545	3.315074	2.7976080	47	3929.4520	2.644213	4.679674	1.7287210
7	898.8070	2.817562	3.342159	2.7808160	48	3964.2141	2.642927	4.738369	1.6910720
8	1011.8094	2.806659	3.368486	2.7637190	49	3997.1805	2.641717	4.799636	1.6529430
9	1123.1365	2.796649	3.394257	2.7463040	50	4028.3912	2.640581	4.863656	1.6143420
10	1232.7669	2.787393	3.419625	2.7285620	51	4057.8873	2.639515	4.930628	1.5752760
11	1340.6786	2.778786	3.444712	2.7104790	52	4085.7112	2.638518	5.000773	1.5357500
12	1446.8499	2.770744	3.469619	2.6920430	53	4111.9060	2.637586	5.074337	1.4957680
13	1551.2586	2.763203	3.494429	2.6732410	54	4136.5159	2.636718	5.151599	1.4553300
14	1653.8824	2.756107	3.519216	2.6540580	55	4159.5855	2.635910	5.232870	1.4144360
15	1754.6993	2.749412	3.544045	2.6344800	56	4181.1602	2.635159	5.318502	1.3730840
16	1853.6868	2.743082	3.568976	2.6144920	57	4201.2860	2.634464	5.408892	1.3312720
17	1950.8228	2.737085	3.594062	2.5940810	58	4220.0093	2.633817	5.504495	1.2889960
18	2046.0852	2.731395	3.619355	2.5732300	59	4237.3771	2.633219	5.605822	1.2462570
19	2139.4523	2.725987	3.644905	2.5519260	60	4253.4370	2.632672	5.713462	1.2030530
20	2230.9024	2.720841	3.670758	2.5301550	61	4268.2374	2.632173	5.828084	1.1593890
21	2320.4145	2.715941	3.696962	2.5079010	62	4281.8274	2.631724	5.950457	1.1152700
22	2407.9682	2.711270	3.723562	2.4851510	63	4294.2570	2.631323	6.081464	1.0707100
23	2493.5435	2.706814	3.750604	2.4618900	64	4305.5769	2.630962	6.222125	1.0257240
24	2577.1216	2.702561	3.778136	2.4381040	65	4315.8391	2.630640	6.373622	0.9803370
25	2658.6844	2.698500	3.806204	2.4137790	66	4325.0961	2.630352	6.537329	0.9345780
26	2738.2149	2.694621	3.834857	2.3889030	67	4333.4017	2.630096	6.714860	0.8884840
27	2815.6975	2.690915	3.864145	2.3634620	68	4340.8102	2.629870	6.908113	0.8420970
28	2891.1180	2.687374	3.894117	2.3374450	69	4347.3766	2.629671	7.119348	0.7954670
29	2964.4639	2.683990	3.924828	2.3108390	70	4353.1564	2.629499	7.351277	0.7486470
30	3035.7242	2.680758	3.956331	2.2836360	71	4358.2052	2.629352	7.607189	0.7016940
31	3104.8903	2.677671	3.988684	2.2558260	72	4362.5783	2.629226	7.891128	0.6546700
32	3171.9554	2.674723	4.021946	2.2274030	73	4366.3307	2.629118	8.208129	0.6076350
33	3236.9152	2.671909	4.056178	2.1983620	74	4369.5166	2.629026	8.564573	0.5606520
34	3299.7679	2.669224	4.091444	2.1686980	75	4372.1892	2.628949	8.968680	0.5137870
35	3360.5142	2.666664	4.127811	2.1384120	76	4374.4002	2.628886	9.431242	0.4671080
36	3419.1578	2.664224	4.165349	2.1075040	77	4376.1999	2.628834	9.966744	0.4206950
37	3475.7051	2.661900	4.204132	2.0759780	78	4377.6371	2.628793	10.595143	0.3746460
38	3530.1657	2.659688	4.244237	2.0438390	79	4378.7584	2.628761	11.344788	0.3290400
39	3582.5521	2.657584	4.285743	2.0110940	80	4379.6088	2.628736	12.257602	0.2840340
40	3632.8797	2.655584	4.328737	1.9777530					

Figure 2a and figure 2b show in details the difference $\Delta G(v) = G(v) - G_v$ and $\Delta B(v) = \langle B(v) \rangle - B_v$ between the eigenvalues $G(v)$, the expectation values $\langle B(v) \rangle$ deduced from the IPA potential and the « experimental » ones G_v and B_v. Inspection of figure 2a and figure 2b shows that up to about $v = 40$ the IPA potential reproduces the experimental energies within 0.002 cm^{-1} and the rotational constants to about 2×10^{-7} cm^{-1}. Between $v = 40$ and $v = 60$ the differences $\Delta G(v)$ and $\Delta B(v)$ increase to values outside the experimental uncertainties but remain relatively low, the maximum $\Delta G(v)$ being for example $- 0.010$ cm^{-1} for $v = 50$. Beyond $v = 60$ up to $v = 80$ the eigenvalues of the energies agree again with the « experimental » ones, within 0.002 cm^{-1}; but the estimated errors on the computed eigenvalues resulting from the consideration of the entire data field is only 0.0004 cm^{-1}. (The estimations of the errors of the term values as a function of R are not available when using a RKR procedure, but are determined by the IPA method). The expectation values of $\langle B(v) \rangle$ are somewhat higher than the experimental ones by an amount not larger than 5×10^{-6} cm^{-1} (see paragraph 4.3). To summarize, in the region near the dissociation limit, from $v = 60$ to $v = 80$, the IPA potential correctly mimics the quantum calculated eigenvalues : a result which is essential to carry out the evaluation of the dissociation limit energy D_e and of the long range C_n coefficients.

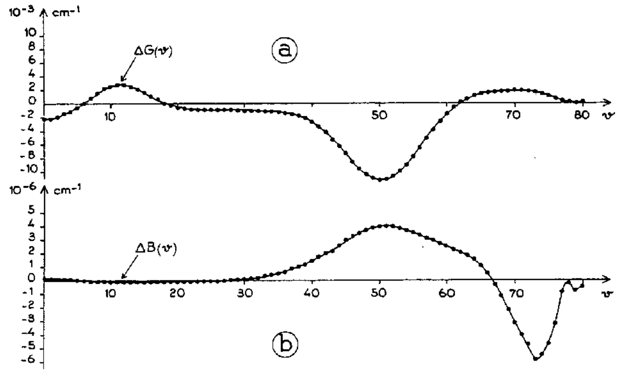

Fig. 2. — a) Differences between the calculated eigenvalues $G(v)$ given in table II and the « experimental » ones described by the Dunham coefficients given in first column of table I. b) Differences between the expectation values $\langle B(v) \rangle$ deduced from the IPA potential (Table II, column 2) and the « experimental » ones described by the Dunham coefficients given in table I, column 2.

3. Determination of the dissociation energy D_e and of the long range C_n coefficients.

From theory [20], it follows that the attractive long range potential should be represented, in the case of the B state of iodine, by the multipole expansion expression :

$$G(v) = D_e - C_n/R_v^n \quad \text{where} \quad n = 5, 6, 8, 10, 12... \quad (1)$$

C_n are positive coefficients [21] to be determined; $G(v)$ is the vibrational term value and R_v is the outer turning point at the energy $G(v)$. $G(v)$ and R_v values used in our analysis are taken from the IPA potential given in table II. Two kinds of parameters may be varied in the analysis : the number of C_n coefficients and the range of sampled R_v values i.e. the number of turning points.

It was already recognized [3] that at least four C_n coefficients with $n = 5, 6, 8$ and 10 must be considered; but at the degree of precision with which the turning points are supposed to be defined (within 4×10^{-4} cm^{-1} according to the uncertainties given at the output of the IPA computing), it is not clear if the C_{12} coefficients may always be neglected. To check this point, we give in table III typical fits encompassing nine turning points (a range in which all the C_n coefficients are positive), with multipole expansion truncated respectively at C_8, C_{10} and C_{12}.

Inspection of table III shows that :

(i) the dissociation limit energy remains sensibly constant whatever the number of C_n coefficients may be;

(ii) the correlation between C_5 and C_6 is well illustrated in this example : when C_5 increases C_6 decreases and the reverse;

(iii) the standard deviations (S.D. last column) remain in good agreement with the errors (4×10^{-4} cm^{-1}) associated to the turning points of the IPA potential, but the S.D. is one order of magnitude lower when the C_{10} coefficient is added;

(iv) when the C_{12} coefficient is introduced, the values of C_{10} and C_{12} are strongly correlated and no more well defined (they may even be negative !); moreover the standard deviation increases slightly instead of decreasing when one more parameter is added. Briefly, adding the C_{12} coefficients does not improve the fits. Thus, in our further analysis, the multipole expansion was limited at maximum up to the C_{10} coefficient.

Least squares fits to a multipole expansion containing four C_n coefficients (C_5, C_6, C_8 and C_{10}) were performed by varying the number of involved turning points. The resulting D_e values are plotted on figure 3a; the standard deviations between the IPA energies $G(v)$ and those recalculated by means of D_e and the long range C_n coefficients are represented on figure 3b. (For sake of completeness D_e values obtained using a multipole expansion truncated at C_8 are also given). It turns out that the dissociation energy D_e is remarkably stable (within 0.001 cm^{-1} !) when the C_{10} coefficient is considered, and increases continuously when the multipole expansion is limited at C_8. Likewise stable behaviour is observed for the C_5, C_6, C_8 and C_{10} coefficients as shown in table IV.

To summarize, the outer branch of the IPA potential can be represented very accurately by means of the multipole expansion truncated at C_{10}, provided that the lowest turning point considered is not lower

Table III. — *Results of least square fits where the multipole expansions were truncated at C_{12}/R_v^{12}, C_{10}/R_v^{10} and C_8/R_v^8, respectively. C_n coefficients are given in $C_n \times 10^{-n}$ Å^n cm^{-1}. The number(s) given in parentheses are the estimated uncertainties corresponding to the last digit(s) of the determinated values.*

v Range	N	D_e (cm^{-1})	10^{-5} C_5	10^{-6} C_6	10^{-8} C_8	10^{-10} C_{10}	10^{-12} C_{12}	S.D. (10^{-3} cm^{-1})
72-80	9	4 381.2600 (14)	3.464 (18)	1.054 (21)	0.450 (4)	—	—	0.30
72-80	9	4 381.2496 (4)	3.168 (12)	1.494 (17)	0.256 (8)	0.040 (2)	—	0.026
72-80	9	4 381.2503 (19)	3.200 (95)	1.44 (2)	0.29 (11)	0.023 (47)	0.003 (8)	0.030

Table IV. — *Results of least squares fits in function of the number N of turning points, using a multipole expansion truncated at* C_{10}/R_v^{10}.

v Range	R_v Range (Å)	N	D_e (cm^{-1})	$10^{-5}\ C_5$	$10^{-6}\ C_6$	$10^{-8}\ C_8$	$10^{-10}\ C_{10}$	S.D. (10^{-3} cm^{-1})
75-80	8.9-12.2	6	4 381.2491 (30)	3.149 (120)	1.52 (20)	0.24 (10)	0.044 (20)	0.04
74-80	8.5-12.2	7	4 381.2491 (10)	3.149 (40)	1.524 (63)	0.24 (3)	0.044 (7)	0.03
73-80	8.2-12.2	8	4 381.2500 (7)	3.181 (21)	1.474 (32)	0.26 (2)	0.038 (3)	0.03
72-80	7.8-12.2	9	4 381.2496 (4)	3.168 (12)	1.494 (17)	0.256 (8)	0.040 (2)	0.03
71-80	7.6-12.2	10	4 381.2491 (4)	3.154 (8)	1.515 (12)	0.246 (5)	0.042 (1)	0.03
70-80	7.3-12.2	11	4 381.2487 (3)	3.142 (7)	1.532 (9)	0.239 (4)	0.0436 (7)	0.03
69-80	7.1-12.2	12	4 381.2492 (3)	3.154 (6)	1.516 (8)	0.246 (3)	0.0423 (6)	0.04
68-80	6.9-12.2	13	4 381.2504 (6)	3.181 (11)	1.477 (15)	0.261 (6)	0.0395 (9)	0.11

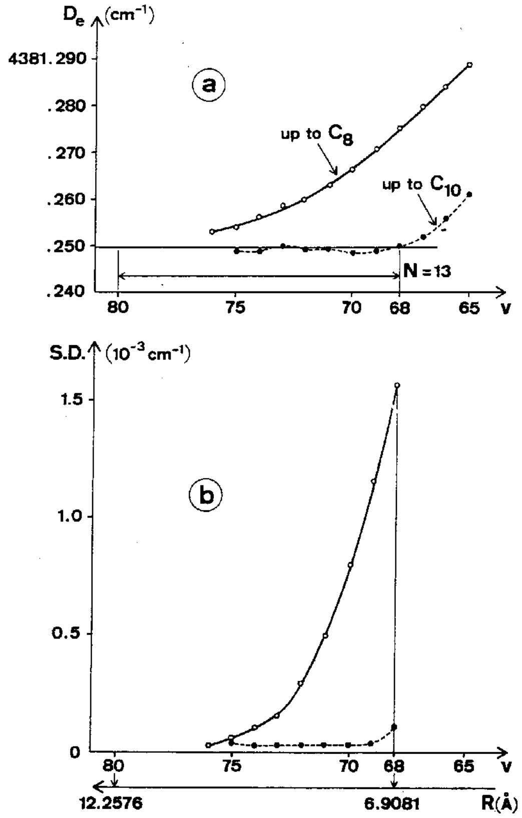

Fig. 3. — a) Variation of the values of the dissociation limit energy D_e as a function of the number N of turning points. For the (68-80) range, $N = 13$. Truncating the multipole expansion at C_8/R_v^8 yields D_e values varying strongly with N. Adding the C_{10}/R_v^{10} term gives D_e values remarkably stable up to $N = 13$.
b) Standard deviations between the calculated eigenvalues $G(v)$ (Table II) and the values recalculated by means of the multipole expansion. Adding the C_{10}/R_v^{10} term reduces the S.D. by two orders in magnitude in the (68-80) range.

than the R_{68} outer point. In this case the dissociation energy $D_e = 4\,381.249_2 \pm 0.001$ cm^{-1} is independent of the number of turning points considered in the R_{68}-R_{80} (7.1-12.2 Å) range.

4. Discussion.

The validity of the results obtained with the use of a simple multipole expansion limited at C_{10}, and without the consideration of the exchange energy $V_{ex}(R)$, must be confirmed by answering to the following quieries :

— Why the addition of the C_{12} coefficient does not improve the fits ?

— What is the influence of the introduction of a R_v^{-11} third order contribution to the energy ?

— To what extent are the D_e and C_n quantities modified by the presence of perturbations in the vicinity of the dissociation limit (Coriolis effect and hyperfine interactions) ?

— Is it justified to retain the results of the fits done with the last outer turning points R_{78}, R_{79} and R_{80}, these points being as « usual » known with less precision ?

These four points will be examined successively and comparison with theoretical estimations of the C_5 and C_6 coefficients will finally be given.

4.1 Addition of the C_{12} coefficient and rôle of the exchange energy $V_{ex}(R)$.

— The exchange energy $V_{ex}(R)$ of the B state of iodine can be estimated from the theoretical work of Gordeev *et al.* [14]. In the notation of these authors the exchange energy has the following expression :

$$V_{ex}(R) = (-\,5.76\,R^3 + 26.5\,R^2 - 32.6\,R) \times \times \exp(-\,2\,\beta R) \quad (2)$$

where $V_{ex}(R)$ and R are in atomic units and $\beta = \sqrt{2\,E_I} = 0.88$, E_I being the ionization potential of the iodine atom. For a multiplet state like the B $^3\Pi_{ou}^+$ state one would expect that the $V_{ex}(R)$ contributions should be repulsive [20] in agreement with results of Gordeev *et al.* Table V gives the calculated values of $V_{ex}(R)$ according to expression (2), together with the expected contributions of the neglected term C_{12}/R_v^{12}. The C_{12} parameter was deduced from a least squares fit with a multipole expansion extended up to C_{12} (as

Table V. — *Comparison between estimated exchange energies* $V_{ex}(R)$ *(after Gordeev* et al. [14]) *and estimation of the* C_{12}/R_v^{12} *contribution deduced from the present work.* (C_{12} *was taken equal to* 0.2836×10^{10} cm^{-1} Å^{12}). *The residuals (column 4) represent* 0.5 % *of the total binding energy at* $R = 9$ Å *(see Fig. 4).*

v	R (Å)	$V_{ex}(R)$ [14] (cm^{-1})	C_{12}/R_v^{12} (cm^{-1})	$V_{ex}(R) - C_{12}/R_v^{12}$ (cm^{-1})
66	7.5373	0.552	0.465	+ 0.087
67	6.7143	0.336	0.337	− 0.001
68	6.908	0.194	0.244	− 0.050
69	7.1193	0.106	0.166	− 0.060
70	7.3512	0.055	0.113	− 0.042
71	7.6071	0.026	0.075	− 0.049
72	7.8911	0.012	0.050	− 0.038
73	8.2081	0.005	0.030	− 0.025
74	8.5645	0.002	0.020	− 0.018
75	8.9686	0.0005	0.010	− 0.009
76	9.4312	0.0002	0.006	− 0.005
77	9.9667		0.003	− 0.003
78	10.5951		0.0014	− 0.0014
79	11.3447		0.0006	− 0.0006
80	12.2257		0.0002	− 0.0002

those given in Table III) but limited to the range v = 72-80, where, according table V, the contribution of $V_{ex}(R)$ remains negligible (~ 0.010 cm^{-1}). Although the C_{12} value is determined with a large uncertainty, the expected contributions are in good agreement with crude extrapolations from the known decreasing C_6/R_v^6, C_8/R_v^8 and C_{10}/R_v^{10} contributions.

The small remaining differences ($V_{ex}(R) - C_{12}/R_v^{12}$) quoted in the last column of table V are easily absorbed partially by D_e and partially by the C_5, C_6, C_8 and C_{10} coefficients within their uncertainties as quoted in table IV. As a result of the least squares fit procedure, one observes very stable D_e values, D_e being less correlated with the C_n coefficients than the C_n coefficients between themselves. The mutual cancellation of the $V_{ex}(R)$ and C_{12}/R_v^{12} contributions explains also why, when adding only C_{12}/R_v^{12} and neglecting $V_{ex}(R)$, the fits are not improved, as observed. The values given in table V are of course only estimation of $V_{ex}(R)$ and C_{12}/R_v^{12}; but our fits show in any way that the values of $V_{ex}(R)$ and C_{12}/R_v^{12} are of the same order of magnitude at least in the v = 67-80 region. The main conclusion is that Gordeev *et al.* estimation of $V_{ex}(R)$ is quite reliable; moreover it is easy to modify slightly, either the β coefficient in expression (2), either the C_{12} coefficient, or both, in order to minimize the differences ($V_{ex}(R) - C_{12}/R_v^{12}$).

4.2 Introduction of a C_{11}/R_v^{11} term. Effective long-range coefficients. — When one tries to introduce the C_{11}/R_v^{11} term in the multipole expansion, which is the third order dipole-quadrupole-dipole dispersion energy [20], the results of the least squares fits are disappointing. In this case, the C_{10} and C_{11} coefficients appear alternatively positive and negative depending on the number of turning points considered. The reason is the strong correlations between contributions which are weak ones. This situation is quite general in multipole fits. When the contributions are weak, C_n and C_{n+1} coefficients cannot be determined unambiguously. Moreover, even for C_n and C_{n+2}, if the contributions of these terms are too weak, the uncertainties become rather large as for example for C_{10} and C_{12} (Table III). The two C_n and C_{n+2} coefficients may be replaced by some average weighted value between C_n and C_{n+2} which, in this case, play the rôle of an effective coefficient. We may even apply this rule for the C_8 and C_{10} coefficients as follows : for example the contributions of the C_8/R_v^8 and C_{10}/R_v^{10} terms are equal to 0.585 and 0.126 cm^{-1} which represent respectively 6 % and 1.3 % of the total binding energy at R = 8.968 Å (v = 75) (Fig. 4). A least squares fit by means of a multipole expression with only four parameters (D_e, C_5, C_6 and C_9'), where C_9' plays the rôle of an « effective » parameter, should be sufficient to describe accurately the potential curve. Table VI gives the results of these fits as a function of the number of considered turning points. In this case, as in the fits with five parameters, the dissociation limit D_e remains almost constant and equal to 4 381.247 ± 0.001 cm^{-1}, a value very close to the value 4 381.249$_2$ ± 0.001 cm^{-1}

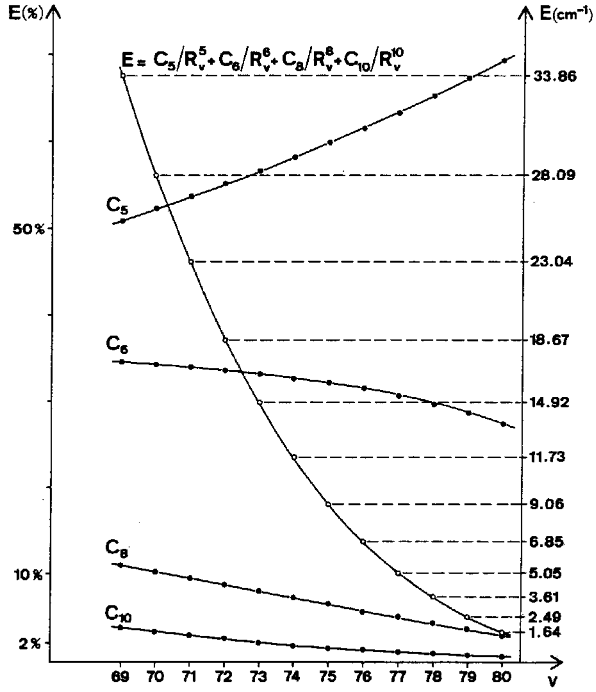

Fig. 4. — Contributions (in %, right side) of the C_n/R_v^n terms (with n = 5, 6, 8 and 10) to the total binding energy E given in cm^{-1} (left side).

Table VI. — *Results of least squares fits in the case where the $C_8/R_v^8 + C_{10}/R_v^{10}$ terms are replaced by an effective C_9'/R_v^9 term.*

v Range	R_v Range (Å)	N	D_e (cm^{-1})	$10^{-5}\ C_5$	$10^{-6}\ C_6$	$10^{-9}\ C_9'$	S.D. ($10^{-3}\ cm^{-1}$)
76-80	9.4-12.2	5	4 381.2475 (9)	3.050 (18)	1.716 (21)	0.189 (4)	0.04
75-80	8.9-12.2	6	4 381.2475 (4)	3.050 (6)	1.716 (7)	0.189 (1)	0.03
74-80	8.5-12.2	7	4 381.2475 (2)	3.047 (3)	1.721 (4)	0.1881 (6)	0.03
73-80	8.2-12.2	8	4 381.2468 (3)	3.039 (4)	1.729 (4)	0.1866 (5)	0.05
72-80	7.8-12.2	9	4 381.2466 (2)	3.034 (3)	1.734 (3)	0.1860 (4)	0.05
71-80	7.6-12.2	10	4 381.2464 (2)	3.033 (2)	1.736 (2)	0.1858 (2)	0.05
70-80	7.3-12.2	11	4 381.2464 (1)	3.033 (1)	1.735 (1)	0.1858 (2)	0.05
69-80	7.1-12.2	12	4 381.2463 (1)	3.032 (1)	1.737 (1)	0.1857 (1)	0.05
68-80	6.9-12.2	13	4 381.2459 (3)	3.028 (2)	1.740 (2)	0.1852 (2)	0.13

obtained when the C_8 and C_{10} coefficients are explicitly taken into account. Likewise the C_5, C_6 and the effective C_9' coefficients remain stable all the way of the 68-80 range. Moreover the S.D. (last column Table VI) are almost the same that the S.D. given in table IV.

However, noticeable differences appear between the C_5 values (3.16 and 3.04 × 10^5 Å^5 cm^{-1}) and the C_6 values (1.51 and 1.72 × 10^6 Å^6 cm^{-1}), which are outside the quoted uncertainties. For this example, we can infer that the C_{10} coefficient obtained in our fits (Table IV) has also to be considered as an « effective » coefficient which absorbs what remains from the higher C_n/R_v^n contributions with $n \geqslant 11$. Neglecting this higher contribution will be without any consequence on the value of the dissociation limit D_e; but through the correlations effects the C_8, and to a lower extent the C_5 and C_6 coefficients will be somewhat altered by an amount certainly much smaller than those encountered in the above example. Thus, the values of the C_{10} coefficient given in table IV represent upper limits of this coefficient and neglecting the R^{-11} contributions is not a catastrophe, as much as we keep in mind that the exchange energy has the opposite sign.

4.3 Presence of perturbations in the vicinity of the dissociation limit.

4.3.1 *Coriolis coupling.* — The Coriolis coupling of the 1_u states (which have the same ($^2P_{3/2}$ + $^2P_{1/2}$) dissociation limit than the B state) and of the B state causes an heterogeneous rotational perturbation which compresses the rotational structure [15] : the experimental values would be smaller than those predicted by a simple mechanical model [19]. When the potential curve of the B state is built up by the RKR method, this perturbation induces errors on the rotationless potential curve since, in the RKR method, the rotational constants play a major rôle. In contrast, in the IPA method, the B_v values are not directly involved; only the energies of rotational levels are required (1) and one may assume that the extrapolated rotationless potential curve for $J = 0$ is almost free from errors due to Coriolis effects. Accordingly, the expectations values of B_v could be somewhat higher than the experimental ones, which is indeed the case in the v = 60-80 region (see Fig. 2b); while the eigenvalues deduced from the IPA potential are in agreement with the « experimental » G_v value (see Fig. 2a), as it should be.

4.3.2 *Hyperfine interactions.* — At the band heads, the separation between fine and hyperfine structures are of the same order of magnitude — we are in presence of super hyperfine structure where only F remains a good quantum number [22, 23] and indeed we have not been able to resolve the origins of the (v, 0) bands when $v \geqslant 76$ [24]. However, the vibrational energies for the levels situated near the dissociation limit are not observed energies but extrapolated values based on higher J levels ($J \geqslant 6$) where perturbations of this kind are minimized; thus, in this way, these extrapolated vibrational energies do not correspond to the actual values of the band origins but represent rather values close to vibrational energies « free » from hyperfine perturbations.

It remains the mixing between u and g states which happens through hyperfine interactions [23, 25, 20]. Fortunately, they are relatively weak and do not prevent to observe in the absorption spectrum bands structure and iodine narrow lines (~ 0.030 cm^{-1} the common line width of iodine lines) up to $v = 80$. For example in the case of the (77,0) bands the B_v value of the perturbing state 1 g was found to be 0.0040(2) cm^{-1} [23], while the observed B_{77}' value is 0.00420(1) cm^{-1}. A mixing of at maximum 14 % [23] between these two close values of B_v and B_{77} does not

(1) The influence of the Coriolis effects on the energies of the rotational levels considered is lower than the experimental uncertainties (see Ref. [19], Table I).

have a discernable effect, at least at the precision of our measurements which was of the order of 0.005 cm^{-1} (~ 150 MHz) in this region [24].

Nevertheless, the analysis made by Broyer *et al.* [25] and recently by Pique *et al.* [23] show that the extrapolated potential beyond $v = 80$ level has to be redefined. Due to the hyperfine structure of the separated atoms $^2P_{3/2}$ and $^2P_{1/2}$ [26] there exists several distinct dissociation limits [20]. Thus, we end with a paradox : the dissociation limit D_e which is the most accurate value determined from the long range potential analysis, because D_e is very weakly correlated with the C_n coefficients, has no more a simple signification (this was already pointed out in the laser induced work [24]). On another hand, the values of the C_n coefficients which are strongly correlated and then determined with a lower precision, keep always their physical signification provided that the quantum mechanical potential curve calculated by means of the IPA method is not biased by hidden perturbations of different kinds.

The fact that the eigenvalues and expectation values of $\langle B(v) \rangle$ deduced from the IPA potential agree with the experimental G_v and B_v values shows that, within the experimental uncertainties which are rather large (a few 10^{-3} cm^{-1} in comparison of sub-Doppler MHz measurements), the IPA potential and their associated errors estimation on the eigenvalues for a given R_v can be considered to be the « true » quantum mechanical potential of the B state in the studied region.

4.4 COMPARISON WITH THEORETICAL ESTIMATIONS OF THE C_5 AND C_6 LONG-RANGE COEFFICIENTS.

4.4.1 *Results of the present work* (*line one and two of Table* VII). — IPA long range analysis yields to nearly identical results if the outer turning points are limited either to R_{80} or R_{77}. The only difference comes from the larger uncertainties associated with the D_e and C_n coefficients on the latter case than in the former. In both cases the S.D. are deemly lower (0.04 and 0.06 × 10^{-3} cm^{-1}) than the IPA estimated errors on the calculated eigenvalues (0.4 × 10^{-3} cm^{-1}). That simply reflects the fact that we are fitting only 12 turning points by means of five parameters. However, doubling the number of points defining the IPA potential in the range $v = 69$-80 does not significantly improve the results given in table VII and the S.D. remains low (0.14 × 10^{-3} cm^{-1}). It should also be emphasized that the uncertainties quoted in table VII must not be considered too seriously; indeed in the fits some fraction of the unknown residuals ($V_{ex}(R) - C_n/R_v^n$) when $n \geqslant 11$ are absorbed by D_e and the remaining part by the coefficients C_n ($n = 5$, 6, 8 and 10) as mentioned in paragraph 4.1.

Briefly, the observation of stable values of D_e and C_n as those given in table IV is a necessary condition in outer turning points analysis, but is not a sufficient one to be sure that the results from the least squares fits are the very true ones, as long as the exchange energies are not accurately known. However, at present time, we can assume that, thanks the mutual cancellation of the $V_{ex}(R)$ and C_{12}/R_v^{12} contributions, even if it is not complete, the values of D_e and C_n can be safely adopted. But their associated uncertainties must be considered to have only the usual mathematical signification in least-squares fits.

4.4.2 *Comparison with theoretical values* (*Table* VII). — The lowest theoretical value of C_5 expressed in term of expectation value $\langle r_{5p}^2 \rangle$ ($C_5 = 0.96 \langle r_{5p}^2 \rangle$ in a.u.) is the one which corresponds to $\langle r^2 \rangle$ estimate from Slater's orbitals.

Other theoretical estimates of $\langle r_{5p}^2 \rangle$ are given in table VII; these values yield always C_5 values higher than the experimental value (3.161) given in table VII by an amount of about 7-15 %. Like wise the theoretical values of C_6 [15], [17] are also higher than the experimental ones.

The « theoretical » potential given by the expression

$$[E(I\,^2P_{3/2}) + E(I\,^2P_{1/2}) - C_5/R_v^5 - C_6/R_v^6] \quad [17]$$

where C_5 and C_6 are taken respectively equal to their calculated values 3.59 × 10^5 cm^{-1} Å^5 and 1.77 × 10^6 cm^{-1} Å^6, is represented by open circles on figure 5. The agreement between the theoretical potential and the « experimental » one (full circles, $D_e - C_5/R_v^5 - C_6/R_v^6 - C_8/R_v^8 - C_{10}/R_v^{10}$) increases with R, as expected. Above $R = 11$ Å ($v = 78$) the discrepancy between the two curves is ≃ 0.2 cm^{-1}

Table VII. — *Final results and comparison with theoretical values.*

v Range	R_v Range (Å)	N	D_e (cm^{-1})	10^{-5} C_5	10^{-6} C_6	10^{-8} C_8	10^{-10} C_{10}	S.D. (10^{-3} cm^{-1})
69-80	7.1-12.25	12	4 381.2492 (3)	3.154 (6)	1.516 (8)	0.246 (3)	0.0423 (6)	0.04
69-77	7.1-9.96	9	4 381.2497 (26)	3.161 (33)	1.506 (43)	0.248 (14)	0.0418 (23)	0.06
Theoretical values : $C_5 = 0.96\,(\langle r_{5p}^2 \rangle)^2$ u.a.			$\langle r_{5p}^2 \rangle$ (Å^2)					
			2.07 [14]	4.52				
			1.745 [16]	3.39	1.79			
			1.796 [17]	3.59	1.77			
			Cummings [15]		1.85			

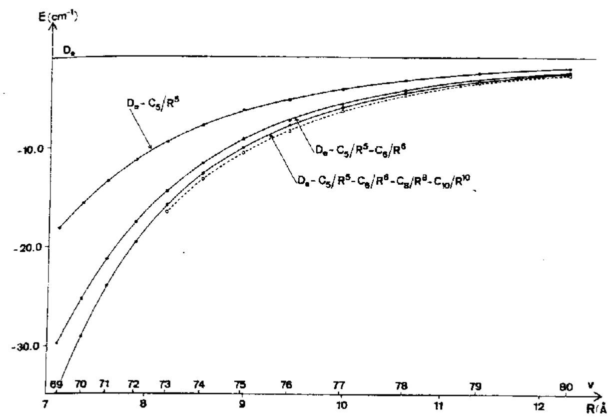

Fig. 5. — Comparison between experimental (full lines, this work) and theoretical (dotted line [17]) potentials near the dissociation limit.

and reaches a value of 0.5 and 0.8 cm^{-1} for $R = 8.2$ Å ($v = 73$) and for $R = 7.2$ Å ($v = 69$) respectively. The addition of C_8/R_v^8 and C_{10}/R_v^{10} terms to the « theoretical » expression of the potential should increase these discrepancies.

A possible way to improve the agreement between theory and experiment would be to assume that, through the strong correlations between the C_n coefficients, our C_8 and C_{10} determinations are somewhat too high which reduce the values of C_5 and C_6. Only theoretical calculations of the C_8 and C_{10} coefficients as well as a new estimation of the exchange energies will make more meaningful fits where C_5 and C_6 should be taken *a priori* as known quantities. But, at present time, the problem of breaking up the strong correlations between the C_n coefficients remains open.

5. Conclusion.

The determination of the quantum mechanical potential of the B state of iodine by means of the IPA method enables us to make a very reliable analysis of the long range part of the potential. In particular, the values of the dissociation limit energy D_e and the long range C_n coefficients (with 5, 6, 8 and 10) are no more depending on the number of turning points considered, a result never reached with the semi-classical first order RKR potential [2].

The reliability of the C_6, C_8 and C_{10} coefficients are not only attested by their high degree of precision, but also by the fact that these coefficients satisfy simultaneously the double inequalities : $R_{69} > (2\ C_{10}/C_8)^{1/2}$ and $R_{69} > (2\ C_8/C_6)^{1/2}$ (the Kreek, Pan and Meath criterium), R_{69} being the lowest turning points considered in the $R = 7.1$-12.22 Å range ($v = 69$-80). Indeed, as recalled by Le Roy [3], and following Kreek, Pan and Meath [30], [31] the « C_{n+2}/R_v^{n+2} » term belonging to the same second order interaction energies no longer represents the appropriate interaction energies at distances R_v smaller than $(2\ C_{n+2}/C_n)^{1/2}$. This means that the C_6, C_8 and C_{10} coefficients and the lower R_v values involved in each fit must satisfy simultaneously the two inequalities :

$$R_v > (2\ C_8/C_6)^{1/2} \quad \text{and} \quad R_v > (2\ C_{10}/C_8)^{1/2}\,.$$

The experimental values of C_5 and C_6 are in good agreement with theory; but for a definitive confirmation, theoretical evaluation of C_8 and C_{10} are needed. However, the C_n coefficients are highly correlated and breaking up these correlations by means of a theoretical background remains a challenge.

The fact that the dissociation limit D_e remains remarkably constant (within 0.001 cm^{-1}), whatever the number of turning points considered (above $R = 7$ Å), is the best illustration of the improvement provided by the IPA rotationless potential up to $v' = 80$, a level located only 1.64 cm^{-1} below the dissociation limit (Fig. 4). Thus this potential seems to escape, at least at « Doppler » spectroscopy scale, from the genuine perturbations present in this region. However the physical signification of the « precise » dissociation limit D_e would have to be redefined in the light of recent hyperfine studies near the dissociation limit [23]. It should be emphasized that the results presented here were obtained using a simple multipole expansion expression truncated at C_{10}, without recourse to damping functions [27], or making assumptions on the behaviour of the neglected contributions from higher inverse power terms than C_{10}/R_v^{10} [3, 28, 29]. But, it is also important, for sake of completness, to add that Leroy's « recommended » C_n values ($n = 5$, 6, 8 and 10) agree fairly well with the results obtained in the present work (see Ref. [3], Tables 2 and 3).

Acknowledgments.

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