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Isotope Shift of He 2*P*

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The isotope shift of the deepest ^3P and ^1P levels of the helium atom is calculated by making use of the wave functions which were reported by one of the authors. The theoretical values of the specific isotope shift of the ^3P and ^1P levels are -636.00×10^{-3} cm^{-1} and 453.83×10^{-3} cm^{-1}, respectively, which are in fairly good agreement with the observed values $(-642\pm5)\times10^{-3}$ cm^{-1} ($2\,^3P$) and $(461\pm5)\times10^{-3}$ cm^{-1} ($2\,^1P$).

1. INTRODUCTION

THE isotope shift of the $S-P$ and $D-P$ lines of helium was measured by Andrew and Carter,[1] Bradley and Kuhn,[2] Fred, Tomkins, Brody, and Hamermesh,[3] and Brochard, Chantrel, and Jacquinot.[4] A theoretical interpretation of the shift was given by Hughes and Eckart,[5] but the calculated values based on their theory were not in good agreement with experiment.[2,3]

The normal shift is simply proportional to the observed wave number of the lines, while the specific shift depends on the initial and final wave functions of the transition. From the theoretical viewpoint we are therefore more interested in the specific shift. Stone[6] calculated the specific shift of He $2\,^{1,3}S$ by making use of Huang's and Hylleraas-Undheim's wave functions. He found agreement within 25% of theory with experiment.

The $2P$ levels are most suitable for comparison between theory and experiment because the specific isotope shift of these levels is expected to be largest and consequently can be calculated and measured most easily. In the present paper this shift will be calculated by making use of the wave functions which were reported by one of the present authors.[7] We shall find that the theoretical values are in fairly good agreement with experiment.

2. WAVE FUNCTIONS

The method of selecting the variational wave function of the excited states of the helium atom was discussed in A,[7] and the wave functions for the deepest ^3P and ^1P states were determined. They are given by the linear combination of four functions,

$$\psi=\sum_{k=0}^{3}a_k\psi_k, \tag{2.1}$$

where all functions are normalized as follows:

$$\|\psi\|=\|\psi_k\|=1,\quad (k=0,1,2,3). \tag{2.2}$$

The basic functions are given by

$$\psi_0=2^{-\frac{1}{2}}(1\mp P)F(\kappa,\mu;r_1,r_2)Z_{sp}, \tag{2.3}$$

$$\psi_1=2^{-\frac{1}{2}}(1\mp P)G(\kappa,\mu_1;r_2,r_1)Z_{sp}, \tag{2.4}$$

$$\psi_2=2^{-\frac{1}{2}}(1\mp P)F(\kappa,\mu_2;r_1,r_2)Z_{sp}, \tag{2.5}$$

$$\psi_3=2^{-\frac{1}{2}}(1\mp P)G(\kappa,\mu_3;r_1,r_2)Z_{pd}, \tag{2.6}$$

where P is the exchange operator; $1-P$ corresponds to the triplet and $1+P$ to the singlet. Z_{sp} and Z_{pd} are the normalized angular functions of the P state corresponding to the *sp* and *pd* configurations, respectively,

$$Z_{sp}=Y_{00}(\omega_1)Y_{1m}(\omega_2), \tag{2.7}$$

$$\begin{aligned}Z_{pd}=(20)^{-\frac{1}{2}}\{&[2(2-m)(2+m)]^{\frac{1}{2}}Y_{10}(\omega_1)Y_{2m}(\omega_2)\\&-[(2-m)(3-m)]^{\frac{1}{2}}Y_{11}(\omega_1)Y_{2m-1}(\omega_2)\\&-[(2+m)(3+m)]^{\frac{1}{2}}Y_{1-1}(\omega_1)Y_{2m+1}(\omega_2)\},\end{aligned} \tag{2.8}$$

where $Y_{lm}(\omega)$ is the normalized spherical surface harmonic corresponding to the azimuthal quantum number l and the orbital magnetic quantum number m, and ω stands for spherical surface coordinates θ and φ. The radial functions are defined by

$$F(\kappa,\mu;r_1,r_2)=N_F(\kappa,\mu)r_2e^{-(\kappa r_1+\mu r_2)}, \tag{2.9}$$

$$G(\kappa,\mu;r_1,r_2)=N_G(\kappa,\mu)r_<r_2e^{-(\kappa r_1+\mu r_2)}, \tag{2.10}$$

where $r_<$ denotes the smaller one of r_1 and r_2, and $N_F(\kappa,\mu)$ and $N_G(\kappa,\mu)$ are the normalization constants. The values of the parameters are shown in Table I.

3. ENERGY LEVEL

The accuracy of the wave function can roughly be estimated by comparing the expectation value of the energy with experiment. If we neglect the kinetic energy of the nucleus, the nonrelativistic Hamiltonian of the He atom is given by

$$H_\infty=-\tfrac{1}{2}(\Delta_1+\Delta_2)-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{r_{12}}, \tag{3.1}$$

where all quantities are measured in atomic units.

The radial function G has a cusp at $r_1=r_2$. Strictly speaking, such a function does not belong to the domain

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[1] A. Andrew and W. W. Carter, Phys. Rev. **74**, 838 (1948).

[2] L. C. Bradley and H. Kuhn, Nature **162**, 412 (1948); Proc. Roy. Soc. (London) **A209**, 325 (1951).

[3] Fred, Tomkins, Brody, and Hamermesh, Phys. Rev. **82**, 406 (1951).

[4] Brochard, Chantrel, and Jacquinot, J. phys. radium **19**, 515 (1958).

[5] D. J. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930).

[6] A. P. Stone, Nature **176**, 130 (1955); Proc. Phys. Soc. (London) **68**, 1152 (1955).

[7] G. Araki, Kgl. Norske Videnskab. Selskabs, Forh. **30**, 158 (1957); Festskrift Til E. Hylleraas På Sekstiårsdagen 15de Mai 1958. This will be referred to as A.

of the kinetic energy (operator). In order to avoid this difficulty we modify the radial function in the immediate vicinity of the cusp so that the derivative becomes continuous. We can choose the vicinity as small as we wish. This is practically equivalent to modifying the definition of the matrix element of Δ in the following way: If φ (a one-electron function) is continuous and ψ has a cusp, we define the Hermitian inner product of φ and $\Delta\psi$ by

$$(\varphi,\Delta\psi)=\lim_{\epsilon\to 0}\int \varphi^*\Delta\psi_\epsilon d(x,y,z), \tag{3.2}$$

where the argument of d indicates the integration variable, ψ_ϵ is the modified function, and ϵ is the length of the vicinity in question. This modification guarantees the Hermiticity of Δ and $i\nabla$ in the followlng sense:

$$(\varphi,\Delta\psi)=-(\nabla\varphi,\nabla\psi)=(\Delta\varphi,\psi). \tag{3.3}$$

The detailed points on this consideration together with related problems will be discussed elsewhere.

TABLE I. Wave function parameters.

	${}^3P$	${}^1P$
κ	1.991 185 792	2.003 024 271
μ	0.544 574 887 8	0.482 362 881 4
μ_1	1.654 750 000	0.868 500 000
μ_2	1.975 000 000	1.437 000 000
μ_3	0.967 500 000	1.199 750 000
a_0	0.991 608 392	0.999 952 404
a_1	0.034 105 777 2	−0.007 405 727 30
a_2	0.003 003 987 56	0.000 963 922 308
a_3	−0.017 361 829 1	−0.019 384 822 6

We denote the matrix element of the Hamiltonian with respect to the basic functions given by (2.3)–(2.6) as follows:

$$H_{jk}=(\psi_j,H_\infty\psi_k),\quad j,k=0,1,2,3. \tag{3.4}$$

We can calculate H_{jk} for $k=0$, 2 according to the ordinary definition of the Hermitian inner product, while in other cases we have, for example,

$$H_{11}=\int\psi_1{}^*H_\infty\psi_1 d(\mathbf{x}_1,\mathbf{x}_2)+\int_0^\infty r^3[G(\kappa,\mu_1;r,r)]^2dr \tag{3.5}$$

The second term is a correction arising from the cusp at $r_1=r_2$. We shall refer to such a term as the cusp correction. The values of the matrix element H_{jk} are shown in Table II. The expectation value of H_∞ is given by

$$E_\infty=\sum_{j=0}^{3}\sum_{k=0}^{3}a_ja_kH_{jk}. \tag{3.6}$$

The mass correction arising from the nuclear motion will be calculated in the next section. Its values are shown in Table III. If we add the mass correction to E_∞ we have the energy level of the He atom. This is denoted by E.

TABLE II. Matrix elements of the Hamiltonian and energy values in atomic units.

		${}^3P$	${}^1P$
	H_{00}	−2.130 691 33	−2.122 390 09
	H_{11}	−0.157 797 040	−0.181 742 651
	H_{22}	−1.302 246 83	−1.652 745 68
	H_{33}	0.532 788 159	1.013 382 362
	H_{01}	−0.455 520 839	−0.167 848 971
	H_{02}	−0.827 816 805	−1.038 796 041
	H_{03}	0.041 869 052 4	0.056 130 469 9
	H_{12}	−0.816 763 287	−0.412 138 016
	H_{13}	0.048 215 645 7	0.121 671 222
	H_{23}	0.070 346 734 6	0.178 005 342
	E_∞	−2.132 532 48	−2.123 477 22
He^4	Mass corr.	0.000 283 462	0.000 297 401
	E	−2.132 249 02	−2.123 179 82
	E_{obs}	$-2.132\,968\,6\pm 7\times 10^{-7}$	$-2.123\,637\,3\pm 7\times 10^{-7}$

The calculated values of E_∞ and E together with the observed value[8] E_{obs} of the levels are shown in Table II, where we adopt the energy relation 1 atomic unit $=219\,474.618$ cm^{-1}. We see that E and E_{obs} are in agreement to four places. This indicates a rough measure for the accuracy of the wave function although accuracy for the energy does not necessarily mean accuracy for the isotope shift. The values of E_∞ are not in agreement with the result in A because the cusp correction was not taken into account in A. If we further vary the parameters we can improve the theoretical values of energy in the fifth place. The details of the calculation and the result will be reported elsewhere as we are here only concerned about the isotope shift.

4. MASS CORRECTION

We now consider the effect of the nuclear motion. When the center of mass is at rest, the nonrelativistic

TABLE III. Matrix elements of $\nabla_1\cdot\nabla_2$ and mass corrections in atomic units.

		${}^3P$	${}^1P$
	M_{00}	0.056 125 580 4	−0.037 010 763 6
	M_{11}	−0.070 280 054 1	0.015 611 464 9
	M_{22}	0.983 082 492	−0.644 767 025
	M_{33}	0.120 622 065	−0.177 305 738
	M_{01}	0.311 714 701	−0.062 201 805 9
	M_{02}	0.234 895 882	−0.154 477 571
	M_{03}	0.368 409 361	0.248 126 915
	M_{12}	0.303 517 289	−0.108 987 520
	M_{13}	0.217 492 077	−0.038 232 128 5
	M_{23}	1.131 109 47	1.154 744 10
	$\langle\nabla_1\nabla_2\rangle_{\text{dir}}$	−0.013 061 040 1	−0.009 673 465 6
	$\langle\nabla_1\nabla_2\rangle_{\text{ex}}$	0.077 696 761 7	−0.036 448 593 0
	$\langle\nabla_1\nabla_2\rangle$	0.064 635 721 6	−0.046 122 058 6
	normal	0.000 292 321	0.000 291 079
He^4 mass corr.	specific	−0.000 008 858 84	0.000 006 321 40
	total	0.000 283 462	0.000 297 401

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[8] E_{obs} is derived from the observed value of He^{4+} $1s\ {}^2S_{\frac{1}{2}}$ [C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1], and the observed values of ${}^2S_{\frac{1}{2}}-{}^3P_1$ and ${}^2S_{\frac{1}{2}}-{}^1P_1$ [G. Herzberg, Proc. Roy. Soc. (London) **A248**, 309 (1958)] by eliminating the fine structure.

Hamiltonian of the internal energy of the He atom is exactly given by

$$H=H_\infty-(1+M)^{-1}H_\infty-M(1+M)^{-2}\nabla_1\cdot\nabla_2, \quad (4.1)$$

where the length is measured in $(1+M)M^{-1}$ times atomic units, and other quantities are all measured in atomic units. M is the mass of the nucleus, and H_∞ is given by (3.1). If the eigenfunction of H is denoted by ψ, the eigenvalue of H is given by

$$E=E_\infty-(1+M)^{-1}E_\infty-M(1+M)^{-2}\langle\nabla_1\nabla_2\rangle, \quad (4.2)$$

where E_∞ and $\langle\nabla_1\nabla_2\rangle$ are the expectation values of H_∞ and $\nabla_1\cdot\nabla_2$, respectively. The last two terms represent the effect of the nuclear motion. The second term will be referred to as the normal mass correction, the last term as the specific mass correction, and the sum of them as the total mass correction. The isotope shifts arising from these mass corrections will be referred to as the normal, specific, and total isotope shifts, respectively.

ψ and E_∞ are approximately given by (2.1) and (3.6), respectively. The matrix elements of $\nabla_1\cdot\nabla_2$ with respect to (2.3)–(2.6) are denoted by

$$M_{jk}=(\psi_j,\nabla_1\cdot\nabla_2\psi_k),\quad j,k=0,1,2,3. \quad (4.3)$$

The cusp correction should be taken into account for the calculation of these elements too. The calculated values of M_{jk} are shown in Table III. $\langle\nabla_1\nabla_2\rangle$ is calculated in the same way as (3.6). It consists of two parts, the direct and exchange integrals which are, respectively, given by

$$\langle\nabla_1\nabla_2\rangle_{\mathrm{dir}}=2(a_0M_{03}+a_1M_{13}+a_2M_{23})a_3, \quad (4.4)$$

$$\langle\nabla_1\nabla_2\rangle_{\mathrm{ex}}=\sum_{k=0}^{3}a_k^2M_{kk}+2(a_0a_1M_{01}+a_0a_2M_{02}+a_1a_2M_{12}). \quad (4.5)$$

The origin of the former is the polarization of the s-orbital, but to discriminate the polarization term from the rest is not obvious.[7] The calculated values of these expectation values together with those of the normal, specific, and total mass corrections for He^4 are also shown in Table III. The values of the isotope shift are given in the next section. For these calculations the following observed mass values (in atomic mass units) are adopted[9,10]:

Mass of electron $=5.487\,63\times10^{-4}$,
mass of He^4 atom $=4.003\,875\,0$,
mass of He^3 atom $=3.016\,983\,5_5$.

The cusp correction to the mass correction is very small. The direct integral of $\nabla_1\cdot\nabla_2$ is small as compared with the exchange integral, as is usually expected.

5. ISOTOPE SHIFT

The theoretical values of the specific isotope shift of levels amount to

$$\begin{aligned}\delta(2\,{}^3P)_s&=-636.00\times10^{-3}\ \mathrm{cm}^{-1}\ \text{(theor.)},\\ \delta(2\,{}^1P)_s&=453.83\times10^{-3}\ \mathrm{cm}^{-1}\ \text{(theor.)},\end{aligned} \quad (5.1)$$

where ${}^{3,1}P$ denotes the energy level (i.e., minus the spectral term), and δQ stands for $Q(\mathrm{He}^3)-Q(\mathrm{He}^4)$ for any quantity Q.

TABLE IV. Observed isotope shifts in 10^{-3} cm^{-1} $\delta\nu=\nu(\mathrm{He}^3)-\nu(\mathrm{He}^4)$ denotes the isotope shift of the lines. $(\delta\nu)_n$ and $(\delta\nu)_s$ are the normal and specific isotope shifts of the lines, respectively. $(\delta E_i)_s$ is the specific isotope shift of the initial level.

			Fred *et al.*[a]			Brochard *et al.*[b]		
	λ (A)	$-(\delta\nu)_n$	$-\delta\nu$	$(\delta\nu)_s$	$(\delta E_i)_s$	$-\delta\nu$	$(\delta\nu)_s$	$(\delta E_i)_s$
$3\,{}^3S-2\,{}^3P$	7065	635	−6	641	5	−22	657	21
4	4713	952	297	655	19	303	649	13
5	4120	1089	438	651	15			
6	3867	1160	508	652	16			
7	3732	1202	548	654	18			
8	3652	1228	586	642	6			
$3\,{}^3D-2\,{}^3P$	5875	763	123	640	4	128_5	635	−1
4	4471	1003	360	643	7	366	637	1
5	4026	1114	474	640	4			
6	3819	1174	547	627	−9			
7	3705	1210	592	618	−18			
8	3634	1234	617	617	−19			
						Bradley-Kuhn[c]		
$3\,{}^1S-2\,{}^1P$	7281	616	1046	−430	24	1046	−430	24
4	5047	889	1333	−444	10	1319	−430	24
5	4437	1011	1461	−450	4	1440	−429	25
6	4168	1076	1529	−453	1	1535	−459	−5
8	3935	1140	1606	−466	−12			
$3\,{}^1D-2\,{}^1P$	6678	672	1124	−452	2	1128	−456	−2
4	4921	911	1358	−447	7	1358	−447	7
5	4387	1022	1462	−440	14	1462	−440	14
6	4143	1082	1512	−430	24	1497	−415	39
7	4009	1119	1532	−413	41	1537	−418	36
8	3926	1142	1543	−401	53	1543	−401	53
$2\,{}^3P-2\,{}^3S$	10 830	414	1151	−737				

[a] See reference 3.
[b] See reference 4.
[c] See reference 2. The largest values of their measurement are cited.

The observed values[2–4] of the total isotope shift $\delta\nu$ of $S-P$ and $D-P$ spectral lines are shown in the fourth and seventh columns of Table IV. From these values we can separate the observed values of the specific shift in the following way. Corresponding to (4.2), the wave number ν of spectral lines is given by

$$\nu=\nu_\infty-(1+M)^{-1}\nu_\infty-M(1+M)^{-2}\nu_s, \quad (5.2)$$

where ν_∞ and ν_s are the wave number corresponding to the difference of E_∞ and $\langle\nabla_1\nabla_2\rangle$, respectively. The normal isotope shift of lines is defined by

$$(\delta\nu)_n=-\nu_\infty\delta(1+M)^{-1}. \quad (5.3)$$

From (5.2) and (5.3) we have

$$(\delta\nu)_n=-\nu(2+M)(1+M)^{-1}\delta(1+M)^{-1} \quad (5.4)$$

to good accuracy, where the omitted part is negligibly small. The values of $(\delta\nu)_n$ are shown in the third column of Table IV.

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[9] Cohen, DuMond, Layton, and Rollett, Revs. Modern Phys. **27**, 363 (1955).

[10] Mattauch, Waldmann, Bieri, and Everling, *Annual Review of Nuclear Science* (Annual Reviews, Inc., Palo Alto, California, 1956), Vol. 6, p. 179.

The observed values of the specific shift $(\delta\nu)_s$ can be obtained by subtracting the normal shift from the total shift:

$$(\delta\nu)_s=\delta\nu-(\delta\nu)_n. \tag{5.5}$$

The result is shown in the fifth and eighth columns of Table IV. If we denote the specific isotope shifts of the initial and final levels by $(\delta E_i)_s$ and $(\delta E_f)_s$, respectively, the specific isotope shift of lines is given by

$$(\delta\nu)_s=(\delta E_i)_s-(\delta E_f)_s. \tag{5.6}$$

The contribution to the specific shift of S and D levels only comes from the polarization term of the s orbital, while the main part of the specific shift of P is the exchange integral. Therefore the former must be small as compared with the latter. It may be considered as evidence for this that $(\delta\nu)_s$ is nearly constant for a definite final level.

If we subtract the theoretical values of $-(\delta E_f)_s$ given by (5.1) from the observed values of $(\delta\nu)_s$ in Table IV, we obtain the specific shifts of S and D levels which are shown in the sixth and ninth columns of Table IV. The observed values of $\delta\nu$ mostly contain errors of about 5×10^{-3} cm^{-1} (even 16×10^{-3} cm^{-1} in the largest case). Therefore their last figures are not definitely significant. The values of $(\delta E_i)_s$ indicate only the order of magnitude.

Bradley and Kuhn[2] graphically derived the total shifts of the levels $2\,{}^1P$ and $2\,{}^3S$ from the plot of the measured shift of lines by extrapolation. We obtain the normal shift of levels from the observed spectral term values in the same way as (5.4). The difference of these two kinds of shift represents the specific shift of the levels. Thus we have

$$\delta(2\,{}^1P)_s=(461\pm5)\times10^{-3}\ \text{cm}^{-1}\ \text{(obs.)}, \tag{5.7}$$

$$\delta(2\,{}^3S)_s=(95\pm5)\times10^{-3}\ \text{cm}^{-1}\ \text{(obs.)}. \tag{5.8}$$

Eliminating $\delta(2\,{}^3S)_s$ from $(\delta\nu)_s$ of $2\,{}^3P-2\,{}^3S$ shown in the last line of Table IV, we have

$$\delta(2\,{}^3P)_s=(-642\pm5)\times10^{-3}\ \text{cm}^{-1}\ \text{(obs.)}. \tag{5.9}$$

Comparing (5.1) with (5.7) and (5.9), we see that the agreement between theory and experiment is satisfactory.

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Electron Affinity of O_2

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It is shown, using molecular orbital theory and experimental data, that 0.15 ev is much the more probable of two alternative values for the electron affinity of O_2 which have been considered. Thermochemical evidence favoring a value of 0.9 ev is rather uncertain and should be given less weight.

Burch, Smith, and Branscomb[1] have recently reported an extrapolated experimental threshold value of 0.15±0.05 ev for photodetachment of an electron from O_2^-, in agreement with conclusions of others from experimental work with gas discharges. However, in view of thermochemical evidence surveyed by Pritchard[2] pointing to an electron affinity of about 0.9 ev for O_2, they suggest that these data could be made consistent by the assumption that the photodetachment which they observed occurs from metastable ${}^4\Sigma_g{}^-$ ions with an excitation energy of 0.75 ev (0.9–0.15 ev) above the ${}^2\Pi_g$ ground state of O_2^-. But "if the interpretation of [the thermochemical evidence] should be erroneous," the observed 0.15 ev could be the true electron affinity of O_2.

Strong theoretical reasons can be given against a value as high as 0.9 ev for the electron affinity of O_2 and in favor of a value such as 0.15 ev. Further, it seems unlikely that the proposed[3] low-energy ${}^4\Sigma_g{}^-$ state of O_2^- exists. There seems then to be little doubt that the electron affinity of O_2 is near the value of about 0.15 ev obtained by BSB, and by others from swarm experiments. The justification of these statements follows.

The ground state of O_2^-, using MO's (molecular orbitals) should be of the structure $\cdots\sigma_g{}^2\pi_u{}^4\pi_g{}^3$, ${}^2\Pi_g$. The ${}^4\Sigma_g{}^-$ state suggested by BSB would be formed[3] from a normal ($2s^22p^4$, ${}^3P$) oxygen atom and a (real or virtual) excited state of the O^- ion (the lowest-energy possibility would be $2s^22p^43s$, ${}^4P$). The lowest-energy ${}^4\Sigma_g{}^-$ state obtainable from these would be of the structure $\cdots\sigma_g{}^2\pi_u{}^4\pi_g{}^2\sigma_g{}^*$ with $\sigma_g{}^*$ a Rydberg MO of O_2^- of the type σ_g3s. But it seems rather unlikely that a bound $\sigma_g{}^*$ (or, still less, any other) Rydberg MO exists

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[1] Burch, Smith, and Branscomb, Phys. Rev. **112**, 171 (1958); hereafter referred to as BSB.

[2] H. O. Pritchard, Chem. Revs. **52**, 529 (1953).

[3] Proposed by Bates and Massey (see H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, 1950), second edition, and further discussed and utilized by Y. Inoue, Japan. J. Geophys. (I), **4**, 21 (1957).