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Calculation of transition frequencies for $H_2{}^+$ and its isotopes to spectroscopic accuracy

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Calculations are reported of certain low-lying infrared transition frequencies in $H_2{}^+$, $D_2{}^+$, HD^+, HT^+, and DT^+. They take account of radiative, relativistic, and nonadiabatic effects and are made to the same level of accuracy (0.002 cm^{-1}) as the recent experimental measurements for HD^+; for the (1,0-0,1), (1,1-0,2), and (2,1-1,0) transitions for this molecular ion, the frequencies are 1869.135 (1869.134), 1823.534 (1823.533), and 1856.781 (1856.778) cm^{-1}, where the experimental results are shown in parentheses. We predict that the current values of the mass ratios m_e/m_p and m_e/m_d are good to ±2 in the sixth significant figure. The nonadiabatic energies are based on extremely large basis sets (up to and including 515 basis functions) and required special techniques for solving the generalized eigenvalue equation.

I. INTRODUCTION

In this paper we report calculations of infrared transition frequencies for $H_2{}^+$, $D_2{}^+$, HD^+, HT^+, and DT^+ which include relativistic, radiative, and nonadiabatic effects. The accuracy of the results, of the order of 0.002 cm^{-1}, surpasses that of all previous calculations and this is primarily due to improvements in the calculation of the radiative and nonadiabatic effects. With this accuracy a meaningful comparison can now be made with the experimental values recently determined by Wing *et al.*[1] for HD^+, and the accuracy of the mass ratios used in the calculation can be found. In fact, the experimental and theoretical transition frequencies, where comparison can be made, agree exactly to within the error limits given.

Previously nonadiabatic energies had only been calculated for the two lowest nonrotational levels of these molecular ions,[2,3] this work extends these calculations to the third nonrotational level.

The paper is divided into five parts: (a) the calculation of the adiabatic energies, (b) the calculation of the relativistic and radiative (Lamb shift) corrections, (c) the calculation of the nonadiabatic energies, (d) the synthesis of these results to give the transition frequencies, and (e) a discussion of the results.

In the calculations the following electron (e), proton (p), deuteron (d), and triton (t) mass ratios were used[4]: $m_e/m_p = 0.000\,544\,617$, $m_e/m_d = 0.000\,272\,444$, and $m_e/m_t = 0.000\,181\,920$; and the following atomic units of energy and length[4]: 1 hartree $= 2R_\infty \approx 219\,474.64$ cm^{-1} and 1 bohr $= a_0 \approx 0.529\,177\,06$ Å.

II. ADIABATIC CALCULATIONS

Excluding relativistic and radiative effects the exact Hamiltonian of a one-electron diatomic molecule AB in the center-of-mass system may be written

$$H = H^0 + H' + H'' , \tag{1}$$

where, using atomic units,

$$H^0 = -\tfrac{1}{2}\nabla_e^2 - r_A^{-1} - r_B^{-1} + R^{-1} , \tag{2}$$

$$H' = -\tfrac{1}{2}\mu^{-1}\nabla_R^2 - \tfrac{1}{8}\mu^{-1}\nabla_e^2 , \tag{3}$$

$$H'' = -\tfrac{1}{2}\mu_a^{-1}\nabla_R \cdot \nabla_e . \tag{4}$$

In these equations ∇_e^2 is the Laplacian operator for the electron relative to the *geometric* center of the nuclei, ∇_R^2 is the Laplacian operator for one nucleus relative to the other, and r_A and r_B are the distances of the electron from nuclei A and B, respectively; R is the internuclear separation, $\mu = m_A m_B/(m_A + m_B)$ is the reduced nuclear mass, and $\mu_a = m_A m_B/(m_A - m_B)$. In the last two definitions m_A and m_B are relative to the electron rest mass (m_e) and not to the electron reduced mass μ_e; Colbourn[5] has shown that use of the latter causes negligible changes in spectroscopic properties. The operator in Eq. (4) only participates for heteronuclear diatomic molecules and even then only in nonadiabatic calculations.

The adiabatic calculation proceeds in two parts: first the calculation of a potential energy curve $U(R)$ and then using this curve the solution of the vibrational-rotational Schrödinger equation to give the total vibronic energies.

In the adiabatic approximation $U(R)$ is given by[6]

$$U(R) = \langle \Psi_B | H^0 + H' | \Psi_B \rangle , \tag{5}$$

where Ψ_B are the Born-Oppenheimer (BO) electronic wave functions, i.e., the eigenfunctions of

$$H^0 \Psi_B = E^0(R) \Psi_B . \tag{6}$$

We will restrict ourselves to the electronic ground state. Equation (6) was solved at a series of R values, 0.2, (0.1), 1.6, (0.025), 2.6, (0.1), and 10.0

TABLE I. Adiabatic energies $-E_A$ (in units of 10^{-10} hartrees).

v	N	$H_2{}^+$	$D_2{}^+$	HD^+	HT^+	DT^+
0	0	5 971 384 600	5 987 885 795	5 978 975 086	5 981 756 751	5 991 304 986
1	0	5 871 541 623	5 916 025 815	5 891 806 732	5 899 316 698	5 925 445 826
2	0	5 777 495 552	5 847 113 526	5 809 019 034	5 820 782 739	5 862 053 312
0	1	5 968 731 251	5 986 546 656	5 976 976 577	5 979 977 008	5 990 186 297
1	1	5 869 027 946	5 914 736 685	5 889 899 459	5 897 613 612	5 924 365 312
2	1	5 775 116 763	5 845 873 128	5 807 200 224	5 819 154 090	5 861 010 073
0	2	5 963 445 707	5 983 873 725	5 972 991 518	5 976 426 997	5 987 952 645
1	2	5 864 020 862	5 912 163 613	5 886 096 439	5 894 216 587	5 922 207 908
2	2	5 770 378 623	5 843 397 366	5 803 573 717	5 815 905 632	5 858 927 121

bohrs, increments in R shown in parentheses, by writing Ψ_B as a product of a function of ξ and a function of η, where ξ and η are the usual elliptical coordinates:

$$\xi = (r_A + r_B)/R, \quad \eta = (r_A - r_B)/R\,, \tag{7}$$

and expanding these two functions in terms of Laguerre and Legendre polynomials, respectively.[6] $U(R)$ can be written as

$$U(R) = E^0(R) + \langle \Psi_B H' \Psi_B \rangle\,, \tag{8}$$

and the second term (the adiabatic correction to the BO potential-energy curve) was calculated at the R values given above by the method used in Refs. 6 and 7.

The second part of the adiabatic calculation is the solution of the equation:

$$[-\tfrac{1}{2}\mu^{-1}\nabla_R^2 + U(R) + (2\mu R^2)^{-1}N(N+1) - E_A]F_{v,N}(R) = 0\,, \tag{9}$$

where N is the rotational quantum number apart from electron spin. The eigenvalues E_A are the adiabatic vibronic energies characterized by the N quantum number and v, the vibrational quantum number. Equation (9) was solved using the well-known Numerov-Cooley method[8] and we used as input, values of $U(R)$ spaced at 0.01 bohrs (a smaller spacing, 0.005 bohrs, did not change the results in the tenth significant figure), these were found from the previous $U(R)$ values by a seven-point Lagrangian interpolation scheme.

Values of E_A for $N = 0$, 1, 2 and $v = 0$, 1, 2 are given in Table I and values for certain infrared transition frequencies ν_A (using these E_A) in column 3 of Table V. For HD^+ comparison can be made with the numbers in column 3 of Table VII of Ref. 9; the agreement is perfect. The transition frequencies for $H_2{}^+$, $D_2{}^+$, and HD^+ differ from those reported in Refs. 6 and 7 because of the use of the Numerov-Cooley method rather than the Greenawalt-Dickinson[10] method and the use of different (more recent) nuclear masses. The notation (v,N)-(v',N') is used for all transitions.

III. RELATIVISTIC AND RADIATIVE CORRECTIONS

The relativistic correction to the potential energy curve $U(R)$, to the order α^2, where $\alpha = 1/137.036$ is the fine-structure constant, is given by

$$\Delta U(R) = \langle \Psi_B H_{\text{rel}} \Psi_B \rangle\,, \tag{10}$$

where[11]

$$H_{\text{rel}} = -\frac{\alpha^2}{8}\left[\epsilon - \frac{8\xi}{R(\xi^2-\eta^2)}\right]^2 - \frac{16\alpha^2[(\xi^2+\eta^2)(\xi^2-1)(\partial/\partial\xi) - 2\xi\eta(1-\eta^2)(\partial/\partial\eta)]}{R^3(\xi^2-\eta^2)^2[(4-\alpha^2\epsilon)(\xi^2-\eta^2)+8\alpha^2\xi/R]}\,. \tag{11}$$

In Eq. (11) $\epsilon = -2[E^0(R) - 1/R]$. The integral in Eq. (10) was evaluated numerically using a 96×96 crossed Gauss-Legendre quadrature; details of this calculation have been reported previously.[12] The accuracy of the $\Delta U(R)$ values calculated for R over the range $R = 0.2$–10 bohrs is believed to be at least four significant figures (an order of magnitude better than previous results[11]).

The radiative correction to $U(R)$ for these molecular ions, to second order in the electromagnetic interaction, is given by the formula[13]

$$\Delta U(R) = 1.035 \times 10^{-6}(10.474 - \ln\overline{E})f^2\,. \tag{12}$$

where $\ln\overline{E}$ is the well-known Bethe logarithm ($\overline{E}$ in rydbergs)[14] and is the normalized value of Ψ_B at the nucleus.

Though $\ln\overline{E}$ is the most difficult part of Eq. (12) to calculate it does not vary rapidly, unlike f, with R and it is the variation with R which affects the transition frequencies. Consequently, though we calculated f exactly, we took $\ln\overline{E}$ to be of the form:

TABLE II. Adiabatic-relativistic-radiative energies $-E_{\mathrm{arr}}$ (in units of 10^{-10} hartrees).

v	N	H_2^+	D_2^+	HD^+	HT^+	DT^+
0	0	5 971 441 690	5 987 943 089	5 979 032 270	5 981 813 968	5 991 362 323
1	0	5 871 597 475	5 916 082 203	5 891 862 825	5 899 372 882	5 925 502 329
2	0	5 777 550 306	5 847 169 080	5 809 074 146	5 820 837 985	5 862 109 043
0	1	5 968 788 263	5 986 603 910	5 977 033 701	5 980 034 173	5 990 243 601
1	1	5 869 083 726	5 914 793 035	5 889 955 497	5 897 669 747	5 924 421 784
2	1	5 775 171 450	5 845 928 646	5 807 255 284	5 819 209 291	5 861 065 773
0	2	5 963 502 564	5 983 930 900	5 973 048 525	5 976 484 057	5 988 009 883
1	2	5 864 076 498	5 912 219 888	5 886 152 368	5 894 272 623	5 922 264 317
2	2	5 770 433 178	5 843 452 814	5 803 628 674	5 815 960 740	5 858 982 762

$$\ln\bar{E} = 2.7040 + 0.0481\ R + 0.1951\ R^2 - 0.0898\ R^3 + 0.0114\ R^4 \tag{13}$$

using Fig. 2 of Gersten's paper[13] to determine the coefficients. Our contention that the form of $\ln\bar{E}$ is not critical was confirmed by finding that the first and second vibrational *spacings* for HD^+ were the same to eight significant figures independently of whether Eq. (13) or $\ln\bar{E} = 3.05$ was used. It might be pointed out that the Bethe logarithms for both the hydrogen atom and the hydrogen molecule are also about 3.0.

Equation (9) was now solved again with $U(R)$ corrected for these two (relativistic and radiative) effects and the new eigenvalues E_{arr} are given in Table II. The changes to the transition frequencies for these two effects combined together (Δ_1) are given in column 4 of Table V.

In general the relativistic correction to a transition frequency is of opposite sign and four times as large as the radiative correction and the two together are roughly proportional to the uncorrected frequency. The radiative corrections calculated in this work are somewhat different from those given by Gersten,[13] for example for the first vibrational spacing in HD^+ he predicts a correction of 0.006 cm^{-1}, whereas we find 0.0081 cm^{-1}, this discrepancy is only partly accounted for by our more accurate values of f.

IV. NONADIABATIC CORRECTIONS

To obtain the nonadiabatic corrections one has to return to "square one" and solve completely the exact nonrelativistic nonradiative Schrödinger equation i.e., the full three-particle problem:

$$H\Psi = E_{\mathrm{na}}\Psi\ , \tag{14}$$

where H is the Hamiltonian of Eq. (1), Ψ are wave functions involving explicitly both nuclear and electronic coordinates, and the eigenvalues E_{na} are the nonadiabatic energy levels.

This equation was solved variationally as has been done in the past,[2,3] but in order to obtain spectroscopic accuracy much larger basis sets were used than before. All integrals which were needed were found as in Ref. (3).

The basis functions used in the linear variational expansion of Ψ were of the form

$$\phi_{ijk}(\xi,\eta,R) = \exp(-\alpha\xi)\cosh(\beta\eta)\xi^i\eta^j \times R^{-3/2}\exp(-x^2/2)H_k(x)\ , \tag{15}$$

where $x = \gamma(R-\delta)$, $H_k(x)$ are the usual Hermite polynomials and α, β, γ, and δ are adjustable parameters, and i, j, and k are integers. For the homonuclear molecular ions Ψ took the form:

$$\Psi_{\mathrm{homo}} = \sum_{i=0}^{i_m}\ \sum_{j=0,2}^{j_m}\ \sum_{k=0}^{k_m} c_{ijk}\phi_{ijk}(\xi,\eta,R)\ . \tag{16}$$

Only even powers of η occur due to the molecular symmetry. For the heteronuclear molecular ions Ψ took the form:

$$\Psi_{\mathrm{hetero}} = \Psi_{\mathrm{homo}} + \sum_{i=0}^{i'_m}\ \sum_{j=1,3}^{j'_m}\ \sum_{k=0}^{k'_m} c_{ijk}\phi_{ijk}(\xi,\eta,R)\ , \tag{17}$$

i.e., odd powers of η are now allowed and get mixed with the even powers through the operator H'', see Eq. (4). Since there is no rotational component to our Ψ, we will be limited to the calculation of nonrotational nonadiabatic energy levels. Consideration of rotation would mean replacing Eq. (14) by a set of coupled differential equations.[15]

The linear variational parameters c_{ijk} and ener-

TABLE III. Basis sets for the nonadiabatic calculations.

Basis set number	i_m	j_m	k_m	i'_m	j'_m	k'_m	n
1	6	8	12	3	3	5	356
2	7	10	13	3	3	5	406
3	9	14	15	4	5	6	515

TABLE IV. Nonadiabatic energies $-E_{na}$ (in units of 10^{-10} hartrees).

v	N	H_2^+	D_2^+	HD^+	HT^+	DT^+
0	0	5 971 390 625	5 987 887 820	5 978 979 674	5 981 761 344	5 991 306 615
1	0	5 871 556 758	5 916 031 154	5 891 818 255	5 899 328 131	5 925 450 137
2	0	5 777 518 661	5 847 121 930	5 809 036 794	5 820 800 248	5 862 060 118

gies E_{na} were determined by solving the usual secular equation but because of the size of the basis sets and the fact that the off-diagonal elements in the relevant matrices were not small compared to the diagonal elements, none of the conventional methods were applicable. Instead we used a modified version of the group-coordinate relaxation method. This technique is described in detail elsewhere.[16]

The nonlinear parameters α, β, γ, and δ were chosen (using moderately large basis sets) such as to minimize the lowest energy. With large basis sets (i.e., with much flexibility in the linear coefficients) their values are not critical; the values we used were $\alpha = 1.6$, $\beta = 0.75$, $\delta = 2.1$ (all ions), and $\gamma = 3.0$ (H_2^+), 3.6 (D_2^+), 3.25 (HD^+), 3.45 (HT^+), 3.8 (DT^+).

The major problem was a *logical* way to choose the integers i, j, and k (i.e., the basis functions) rather than blindly adding to the basis set all possibilities. This problem was resolved by discovering that the sum of i, j, and k was a key factor and that basis functions for which this sum was greater than 15 contributed less than 1×10^{-10} hartrees to the energy. Consequently, for Ψ_{homo} i_m, j_m, and k_m (the maximum values of i, j, and k) were raised in unison but with the proviso that terms with

$$i + j + k > 15 \tag{18}$$

were excluded from the expansion. The raising of i_m, j_m, and k_m was continued until the energy of a *particular* level under scrutiny changed by less than 2×10^{-9} hartrees. For the heteronuclear molecular ions the number of additional (odd) basis functions is not very great, hence i'_m, j'_m, and k'_m

TABLE V. Transition frequencies and corrections (in cm^{-1}).

	Transition	ν_A	Δ_1	Δ_2	Δ_3	ν_{total}
H_2^+	(1,0)-(0,0)	2191.3001	0.0272	−0.2000	0	2191.1273
	(2,0)-(1,0)	2064.0728	0.0241	−0.1750	0	2063.9219
	(1,0)-(0,1)	2133.0659	0.0254	−0.2000	0.0038	2132.8951
	(1,1)-(0,2)	2072.2304	0.0236	−0.2000	0.0076	2072.0616
	(2,1)-(1,0)	2116.2811	0.0256	−0.1750	−0.0038	2116.1279
D_2^+	(1,0)-(0,0)	1577.1443	0.0199	−0.0728	0	1577.0914
	(2,0)-(1,0)	1512.4500	0.0183	−0.0672	0	1512.4011
	(1,0)-(0,1)	1547.7536	0.0190	−0.0728	0.0009	1547.7007
	(1,1)-(0,2)	1517.3827	0.0181	−0.0728	0.0019	1517.3299
	(2,1)-(1,0)	1539.6736	0.0191	−0.0672	−0.0009	1539.6246
HD^+	(1,0)-(0,0)	1913.1243	0.0240	−0.1522	0	1912.9961
	(2,0)-(1,0)	1816.9800	0.0216	−0.1369	0	1816.8647
	(1,0)-(0,1)	1869.2621	0.0226	−0.1522	0.0026	1869.1351
	(1,1)-(0,2)	1823.6600	0.0212	−0.1522	0.0052	1823.5342
	(2,1)-(1,0)	1856.8983	0.0227	−0.1369	−0.0026	1856.7815
HT^+	(1,0)-(0,0)	1809.3501	0.0227	−0.1501	0	1809.2227
	(2,0)-(1,0)	1723.6214	0.0204	−0.1334	0	1723.5084
	(1,0)-(0,1)	1770.2893	0.0215	−0.1501	0.0025	1770.1632
	(1,1)-(0,2)	1729.7539	0.0203	−0.1501	0.0050	1729.6291
	(2,1)-(1,0)	1759.3660	0.0215	−0.1334	−0.0025	1759.2516
DT^+	(1,0)-(0,0)	1445.4415	0.0183	−0.0588	0	1445.4010
	(2,0)-(1,0)	1391.3049	0.0170	−0.0548	0	1391.2671
	(1,0)-(0,1)	1420.8892	0.0175	−0.0588	0.0007	1420.8486
	(1,1)-(0,2)	1395.5807	0.0168	−0.0588	0.0014	1395.5401
	(2,1)-(1,0)	1414.2014	0.0176	−0.0548	−0.0007	1414.1635

(the maximum values of i, j, and k for these basis functions) were raised together, as before, but no restriction was placed on the sum of i, j, and k for these functions. The final basis sets (numbered 1, 2, and 3) as used for calculations of the lowest, second lowest, and third lowest nonrotational energy levels, respectively, for the heteronuclear molecular ions are given in Table III. In this table n is the total number of basis functions, i.e., for HD^+, HT^+, DT^+ for the third lowest nonrotational energy level 515 basis functions were used. For the homonuclear molecular ions the same basis sets were used but without the "odd" functions.

Values of the nonadiabatic energies (E_{na}) for the five ions for the three lowest nonrotational states are given in Table IV. Transition frequencies were also calculated and when compared with the corresponding adiabatic transition frequencies gave the vibrational nonadiabatic correction (Δ_2). Values of Δ_2 may be found in column 5 of Table V.

V. TRANSITION FREQUENCIES

In Table V a limited number of transition frequencies, labeled (v,N)-(v',N'), based on the previous calculations are presented. The limitation comes from the fact that nonadiabatic energies were only calculated for the three lowest nonrotational levels.

To obtain the *additional* nonadiabatic corrections for those transitions involving N or $N' \neq 0$, labeled Δ_3 in the table it was necessary to use the approximate formula[9]

$$\Delta_3 = -5.51\times 10^3\left(\frac{0.29}{\mu^2} + \frac{0.56}{\mu_a^2}\right)[N(N+1) - N'(N'+1)] . \tag{19}$$

This approximation is adequate since Δ_3 is quite small. Values of Δ_3 are given in column 6 and values of the total transition frequencies ν_{total} (including all corrections) in the final column where

$$\nu_{\text{total}} = \nu_A + \Delta_1 + \Delta_2 + \Delta_3 . \tag{20}$$

VI. DISCUSSION

Taking into consideration the level of accuracy at each stage of the calculation we believe that the final column of numbers (ν_{total}) in Table V are good to ±0.002 cm^{-1} (the same as the experimental accuracy of Wing *et al.*[1]). They surpass in accuracy all previous calculations. They differ as well from some previous calculations[3] because of the use of different nuclear masses, from others[2,9] because of the larger basis sets used in the nonadiabatic part of the calculation, or because of the recalculation of the radiative corrections. Though corrections due to finite nuclear size[17] and parity violation[18] have not been considered these are thought to be exceedingly small when dealing with transitions.

Three of the transition frequencies we have calculated can be compared directly with experiment, these are (1, 0)-(0, 1), (1, 1)-(0, 2), and (2, 1)-(1, 0) for HD^+, the experimental frequencies are 1869.134, 1823.533, and 1856.778 cm^{-1}, respectively, the corresponding theoretical values are 1869.135, 1823.534, and 1856.781 cm^{-1}. The agreement is within the combined (theoretical and experimental) error bars.

Wing *et al.*[1] have suggested that calculations such as those reported here, when coupled with the experimental data, could lead to a refinement of the values of the mass ratios m_e/m_p, m_e/m_d, m_e/m_t. Since a vibrational spacing (ΔG) is roughly proportional to $\mu^{-1/2}$ it is easy to show that

$$\delta(\mu^{-1}) \simeq 2\mu^{-1}\delta(\Delta G)/\Delta G , \tag{21}$$

and if we allow that, for HD^+, the agreement between experiment and theory is less than 0.002 cm^{-1} then for this molecular ion $\delta(\mu^{-1}) = 1.6\times 10^{-9}$ with the implication that m_e/m_p and m_e/m_d are the values given in the Introduction to within ~2 in the last significant figure.

In Ref. 9 the following approximate formula is given for the vibrational part of the nonadiabatic correction to a given *energy level*:

$$\Delta_v = (X/\mu + \mu Y/\mu_a^2)T_v , \tag{22}$$

where X and Y are constants and the same for all five species and T_v is the vibrational kinetic energy. This means that $\mu\Delta_v/T_v$ should be constant within a given species and the same for H_2^+ as for D_2^+ (since $\mu_a^{-1} = 0$). Using the values of T_v from Table VI,[19] the values of the ratio given in Table VII are found. It is clear that $\mu\Delta_v/T_v$ is only roughly

TABLE VI. Vibrational kinetic energies T_v (in cm^{-1}).

v	H_2^+	D_2^+	HD^+	HT^+	DT^+
0	568.5	404.7	493.8	466.2	370.1
1	1599.2	1160.5	1401.5	1327.3	1065.4
2	2506.1	1852.8	2215.3	2104.6	1707.5

TABLE VII. Values of $\mu\Delta_v/T_v$ (in a.u. of mass, m_e).

v	H_2^+	D_2^+	HD^+	HT^+	DT^+
0	0.2135	0.2015	0.2496	0.2976	0.2126
1	0.1908	0.1853	0.2209	0.2602	0.1954
2	0.1858	0.1826	0.2154	0.2513	0.1926

constant and that use of Eq. (22) could lead to inaccuracies in Δ_v of the order of 10%.

Finally, using an effective Schrödinger equation Bishop[20] has calculated Δ_2 for the pure vibrational spacings in $H_2{}^+$ and $D_2{}^+$, his values for the two lowest spacings 0.20 and 0.17 cm^{-1} for $H_2{}^+$ and 0.08 and 0.07 cm^{-1} for $D_2{}^+$ are in good agreement with the corresponding Δ_2 values in Table V. It should be pointed out, however, that the effective equation contained a variable parameter (k) which was selected such that the lowest energy level of $H_2{}^+$ agreed with an earlier[3] rigorous nonadiabatic calculation.

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