

and by Reynolds *et al.*,²³ Weyl and Phillips²⁴ on H projectiles. The curves for Al and Au combine data taken by Gobeli³⁶ on He and the data of many experimenters with hydrogen beams as collected by Whaling.³⁵

In the high-energy region above 1 MeV per amu, Roll and Steigert, giving fluorine projectiles as a typical example show that $\epsilon_{M, F}/\epsilon_{M, H}$ ratios fall into two groups, one having a common and larger numerical value characteristic of solid targets as a class, and a group, characteristic of gases, having smaller numerical values.

³⁶ G. W. Gobeli, Phys. Rev. **103**, 275 (1956).

Figure 7 indicates that, unfortunately for the usefulness of ϵ_{He}/ϵ_H ratios in this lower energy region, such a grouping into values typical of solids and gases probably does not occur, but that the difference between solids and gases is comparable to the difference between different gases (such as He and Ar) and different metals.

ACKNOWLEDGMENT

Our thanks are due to John Erwood for extensive help in circuit construction and maintenance of the Cockcroft-Walton accelerator.

Dissociation Energy of $He_2^+(^2\Sigma_u^+)$ †

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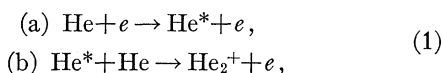
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(Received 17 May 1963)

The potential curve for $He_2^+(^2\Sigma_u^+)$ has been calculated using Slater-type orbitals as a basis for a 26-term atomic orbital-configuration wave function. The calculation establishes a rigorous lower bound, $E_{exp}(atoms) - E_{calc}(molecule)$, of 2.24 eV for the dissociation energy of $He_2^+(^2\Sigma_u^+)$. This value together with the ionization energies of $He^*(2^3S)$ and $He_2^*(^3\Sigma_u^+)$ is used in an energy cycle to give a lower limit of 1.76 eV for the dissociation energy of $He_2^*(^3\Sigma_u^+)$.

INTRODUCTION

THE helium molecule ion He_2^+ was first detected by Tüxen¹ in the mass spectrometer. The results of subsequent mass spectrometric investigations²⁻⁴ have established that its mechanism of formation is



where He^* is some excited state (s) of the helium atom. A lower bound for the dissociation energy of He_2^+ may, therefore, be determined by the equation

$$D_0(He_2^+) \geq I(He) - A.P.(He_2^+), \quad (2)$$

where $A.P.(He_2^+)$ is the appearance potential of He_2^+ in the mass spectrometer. The most recent investiga-

tion⁴ finds

$$D_0 \geq 1.5 \pm 0.3 \text{ eV.}$$

An estimate of the interaction energy of a helium ion and a helium atom can be obtained from the scattering cross sections of the ion into helium gas. Mason and Vanderslice⁵ computed a value of $D_e = 2.16$ eV ($D_e \cong D_0 + 0.1$) by analyzing the scattering data of Cramer and Simons⁶ in terms of a Morse potential. The process of obtaining a potential curve from scattering data involves several uncertainties so that this result cannot on its own merit be regarded as reliable.

A third estimate for the dissociation energy of He_2^+ can be found from the energy cycle,

$$\begin{aligned} D_0(He_2^+(^2\Sigma_u^+)) = D_0(He_2^*(^3\Sigma_u^+)) \\ + I(He^*(2^3S)) - I(He_2^*(^3\Sigma_u^+)). \end{aligned} \quad (3)$$

The last two terms of the right member of Eq. (3) are known with high accuracy. Using a value of $D_0(He_2^*(^3\Sigma_u^+)) = 2.6$ eV, obtained by means of a linear

† Supported by the Robert A. Welch Foundation, Houston, Texas, and the U. S. Air Force Office of Scientific Research, Contract AF-AFOSR-273-63.

¹ O. Tüxen, Z. Physik **103**, 463 (1936).

² F. L. Arnot and M. B. M'Ewen, Proc. Roy. Soc. (London) **A177**, 106 (1939).

³ J. A. Hornbeck and J. P. Molnar, Phys. Rev. **84**, 621 (1951).

⁴ F. J. Comes, Z. Naturforsch. **17a**, 1032 (1962).

⁵ E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **29**, 361 (1958).

⁶ W. H. Cramer and J. H. Simons, J. Chem. Phys. **26**, 1272 (1957).

Birge-Sponer extrapolation of the data of Dieke, Takamine, and Suga,⁷ Herzberg⁸ quotes a value of $D_0(\text{He}_2^+(^2\Sigma_u^+))=3.1$ eV.⁹ [Estimates of this type are generally too high. See Gaydon.⁹]

Ab initio quantum mechanics has now progressed to the point where one can hope, given a situation such as outlined above, to make statements about the dissociation energy which are more accurate than the experimental statements. The variation principle states that a variational calculation of the energy $E_{\text{calc}}(R)$ provides a rigorous upper limit for the energy of the molecule at the separation R . It follows that the quantity D_e^{LB}

$$D_e^{\text{LB}} \equiv E_{\text{exp}}(\infty) - E_{\text{calc}}(R_e) \leq D_e, \quad (4)$$

where $E_{\text{exp}}(\infty)$ is the sum of the experimental atomic energies, provides a rigorous lower limit to the dissociation energy. This quantity is not to be confused with the *rationalized* dissociation energy,

$$D_e^R \equiv E_{\text{calc}}(\infty) - E_{\text{calc}}(R_e), \quad (5)$$

which may lie above or below the true dissociation energy, depending on the relative magnitudes of the errors in $E_{\text{calc}}(\infty)$ and $E_{\text{calc}}(R_e)$.

THE CALCULATION

Ab initio, variational calculations have been made on the ground state $^2\Sigma_u^+$ of He_2^+ and a rigorous lower limit to the dissociation energy D_e^{LB} has been obtained. The calculation was carried out using Slater-type orbitals as a basis for a 26-term atomic orbital configuration wave function $\psi = \sum_{i=1}^{26} c_i \Phi_i$ and the usual nonrelativistic Hamiltonian. The orbital exponents were determined by a procedure described elsewhere.¹⁰ In addition, values of $E(R)$ were computed for a wide range of R (see Table I) and from these the spectroscopic constants for the

TABLE I. Numerical potential energy curve.

R	$E(R)$	R	$E(R)$
10	-4.90141	2.75	-4.96237
9	-4.90145	2.5	-4.97396
8	-4.90155	2.375	-4.97912
7	-4.90188	2.25	-4.98329
6	-4.90302	2.1875	-4.98472
5.5	-4.90437	2.125	-4.98566
5	-4.90686	2.0625	-4.98594
4.5	-4.91151	2.0	-4.98540
4	-4.91923	1.9375	-4.98382
3.5	-4.93192	1.875	-4.98110
3.25	-4.94061	1.75	-4.97084
3	-4.95090	1.5	-4.92109

⁷ G. H. Dieke, T. Takamine, and T. Suga, *Z. Physik* **49**, 637 (1928).

⁸ G. Herzberg, *Spectra of Diatomic Molecules, Molecular Spectra and Structure* (D. Van Nostrand Inc., Princeton, New Jersey, 1950), 2nd. ed., Vol. I.

⁹ A. G. Gaydon, *Proc. Phys. Soc. (London)* **58**, 525 (1946).

¹⁰ Pat N. Reagan, Doctoral dissertation, The University of Texas, 1963 (unpublished).

TABLE II. Spectroscopic constants.

	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$	$10^{-5}k_e$ (dyn/cm)	$\alpha_e(\text{cm}^{-1})$	$B_e(\text{cm}^{-1})$
Herzberg ^a	1627.2	39.2 ^b	3.119	0.23 ^c	7.22
Present calc	1645.7	36.0 ^b 38.8	3.191	0.128	6.99

^a See Ref. 8.

^b These values are not for He_2^+ , but are for the $a^1\Sigma_u^+$ and $e^3\Pi_g$ states, respectively, of He_2^+ .

^c This number is listed by Herzberg (Ref. 8) as uncertain.

ground state were determined using the procedures outlined by Herzberg.⁸

RESULTS

The calculations provide the rigorous lower bound $D_e^{\text{LB}}(\text{He}_2^+)=2.24$ eV and a rationalized dissociation energy of $D_e^R=2.30$ eV. The calculated spectroscopic constants are entered into Table II and are seen to be in excellent agreement with those obtained from analysis of experimental data.

Similar calculations on more complex diatomic systems lead the present authors to estimate that the dissociation energy of He_2^+ should be no more than 0.3 eV greater than the calculated lower bound, 2.24 eV. The dissociation energy D_0 listed by Herzberg⁸ is, therefore, too large. The lower bounds for D_0 estimated by mass spectrometric experiments²⁻⁴ are clearly too small and the estimate of Mason and Vanderslice⁵ is also somewhat small. In Fig. 1 are plotted the potential curves resulting from the present calculation with ap-

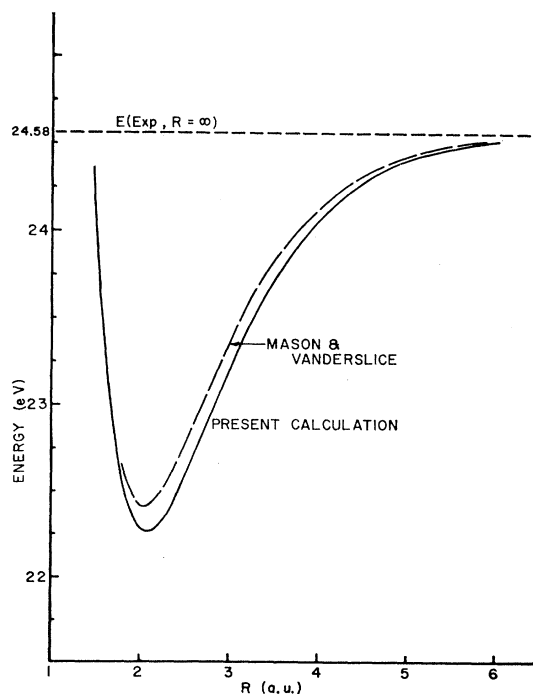


FIG. 1. Comparison of Mason and Vanderslice (Ref. 5) analysis with present calculation using Eq. (5).

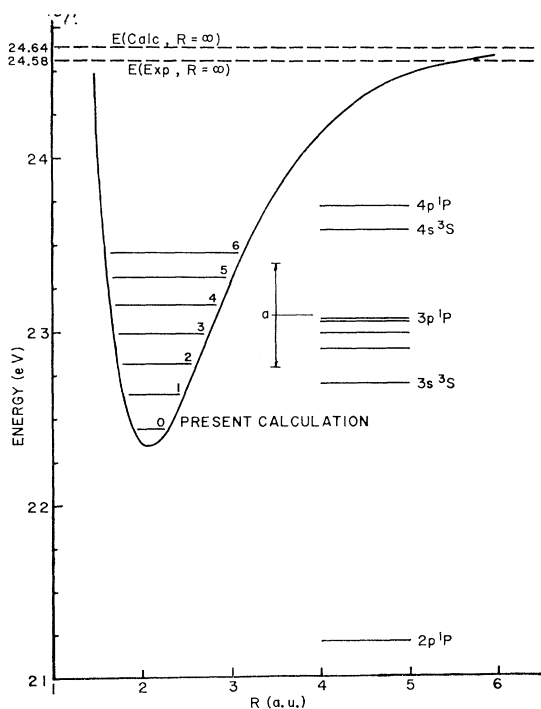


FIG. 2. Potential curve from present calculation using Eq. (4). The appearance potential given by Comes (Ref. 4) is shown as "a" in the figure.

plication of Eq. (5) and from the Morse function obtained by Mason and Vanderslice.⁵

Based on the results of mass spectrometric experiments and also other evidence, Hornbeck¹¹ and Comes⁴ have suggested that the 3^3P or 3^3D excited states of helium are the ones most likely involved in the mechanism of reaction, Eq. (1). Figure 2 illustrates the calculated potential curve (every point of this curve is a rigorous lower bound) together with some vibrational energy levels calculated with the aid of the equation,

$$G(\nu) = \omega_e(\nu + \frac{1}{2}) - \omega_e x_e(\nu + \frac{1}{2})^2,$$

where ω_e and $\omega_e x_e$ are the calculated values listed in Table II; a few of the lower excited states of the helium atom are illustrated in the right-hand margin. The figure clearly illustrates that, at ordinary temperature, helium atom excited states of the second principal quantum level cannot be involved in the mechanism of reaction, Eq. (1), and that all states above the second level are energetically feasible.

One may use Eq. (3) and the present calculated value of $D_e(\text{He}_2^+)$ to determine a lower bound for the dissociation energy of the $\text{He}_2^*(^3\Sigma_u^+)$ which should be in error by the same amount as the present calculated value for He_2^+ . This results in a lower limit of $D_e^{\text{LB}}(\text{He}_2^*(^3\Sigma_u^+)) = 1.76$ eV with a probable upper limit of 2.02 eV.

¹¹ J. A. Hornbeck, Phys. Rev. **84**, 615 (1951).

TABLE III. Previous calculations.^a

Author	$D_e^{\text{LB}}(\text{ev})$	$D_e^{\text{R}}(\text{ev})$	$R_e(\text{au})$
Pauling 1st ^{b,d}	no binding	2.9	1.91
Pauling 2nd	0.05	2.47	2.05
Weinbaum ^e	0.71	2.22	2.07
	(0.68)	(2.21)	(2.15)
Moiseiwitsch 1st ^{b,f}	no binding	3.1	2.1
Moiseiwitsch 2nd		2.0	2.2
	(0.62)	(2.14)	(2.20)
Moiseiwitsch 3rd		1.5	2.5
	(0.83)	(1.59)	(2.33)
Csavinszky ^g	0.84	1.63	2.00 ^e
	(1.00)	(1.74)	(2.23)
Present calc	2.24	2.30	2.06

^a Numbers within parentheses were calculated by the present authors.
^b The Pauling and Moiseiwitsch first calculations are the same; the present authors have confirmed the corrections reported by Moiseiwitsch.
^c The Csavinszky calculation was carried out at the single point, $R = 2$ a.u.
^d L. Pauling, J. Chem. Phys. **1**, 56 (1933).
^e S. Weinbaum, J. Chem. Phys. **3**, 547 (1935).
^f B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A69**, 653 (1956).
^g P. Csavinszky, J. Chem. Phys. **31**, 178 (1959).

PREVIOUS CALCULATION

All previous *ab initio* calculations on the dissociation energy of He_2^+ were carried out using various sets of orbital exponents in a single-term wave function. The results of some previous calculations are listed in Table III. Several of the previous calculations were repeated by the present authors and a few discrepancies were noted; the repeated calculations are listed in Table III within parentheses.

ACKNOWLEDGMENTS

Some preliminary results from this calculation were published in the Journal of the American Chemical Society.¹² The authors wish to express thanks to the University of Texas Computation Center for the vast amounts of computer time necessary for the calculations.

APPENDIX I

Orbital Exponents and Coefficients for $R = 2.0625$ a.u.

$$\delta(1s) = 1.835, \quad \delta(1s') = 1.990, \quad \delta(2s) = 1.910,$$

$$\delta(3s) = 2.210, \quad \delta(2p_0, 3p_0, 3d_0) = 2.070,$$

$$\delta(2p_{\pm 1}, 3p_{\pm 1}, 3d_{\pm 1,2}) = 3.240$$

$c_1 = 0.471984,$	$c_{14} = 0.007676,$
$c_2 = -0.679969,$	$c_{15} = -0.019192,$
$c_3 = -0.305358,$	$c_{16} = 0.013168,$
$c_4 = 0.213010,$	$c_{17} = -0.034893,$
$c_5 = 0.027000,$	$c_{18} = 0.032144,$
$c_6 = 0.401581,$	$c_{19} = 0.040488,$
$c_7 = 0.080983,$	$c_{20} = -0.014895,$
$c_8 = -0.003487,$	$c_{21} = -0.003833,$
$c_9 = -0.015013,$	$c_{22} = 0.004617,$
$c_{10} = -0.070400,$	$c_{23} = -0.004181,$
$c_{11} = 0.023456,$	$c_{24} = 0.043692,$
$c_{12} = 0.007603,$	$c_{25} = 0.013831,$
$c_{13} = 0.008861,$	$c_{26} = -0.014138.$

¹² P. N. Reagan, J. C. Browne, and F. A. Matsen, J. Am. Chem. Soc. **84**, 2650 (1962).

APPENDIX II

Wave Functions

$$\begin{aligned} \mathbf{P} &= \frac{1}{2}(I - i),^{13} \\ (ab:c) &\equiv \det[a(1)\alpha(1)b(2)\alpha(2)c(3)\beta(3)], \\ [(ac)b] &\equiv (ab:c) + (cb:a), \\ \Phi_1 &= \mathbf{P}[(1s_a 1s_a)1s_b'], \\ \Phi_2 &= \mathbf{P}[(2s_a 2s_a)1s_b'], \\ \Phi_3 &= \mathbf{P}[(3s_a 3s_a)1s_b'], \\ \Phi_4 &= 2\mathbf{P}[(1s_a 2s_a)1s_b'], \\ \Phi_5 &= 2\mathbf{P}[(1s_a 3s_a)1s_b'], \\ \Phi_6 &= 2\mathbf{P}[(2s_a 3s_a)1s_b'], \\ \Phi_7 &= 2\mathbf{P}[(2s_a 1s_b')1s_a], \\ \Phi_8 &= \mathbf{P}[(1s_a 1s_a)2s_a], \\ \Phi_9 &= \mathbf{P}[(1s_a 1s_a)3s_a], \end{aligned}$$

¹³ The operator \mathbf{P} produces the ungerade symmetry. I is the identity transformation and i is the inversion through the center of the molecule.

$$\begin{aligned} \Phi_{10} &= \mathbf{P}[(2p_{0a} 2p_{0a})1s_b'], \\ \Phi_{11} &= 2\mathbf{P}[(2p_{+1a} 2p_{-1a})1s_b'], \\ \Phi_{12} &= \mathbf{P}[(1s_a 1s_a)2p_{0a}], \\ \Phi_{13} &= 2\mathbf{P}[(1s_a 2p_{0a})1s_b'], \\ \Phi_{14} &= 2\mathbf{P}[(2s_a 2p_{0a})1s_b'], \\ \Phi_{15} &= \mathbf{P}[(1s_a 1s_a)2s_b], \\ \Phi_{16} &= \mathbf{P}[(1s_a 1s_a)3s_b], \\ \Phi_{17} &= \mathbf{P}[(3p_{0a} 3p_{0a})1s_b'], \\ \Phi_{18} &= 2\mathbf{P}[(3p_{+1a} 3p_{-1a})1s_b'], \\ \Phi_{19} &= 2\mathbf{P}[(2p_{0a} 3p_{0a})1s_b'], \\ \Phi_{20} &= 2\mathbf{P}\{[(2p_{-1a} 3p_{+1a})1s_b'] + [(2p_{+1a} 3p_{-1a})1s_b']\}, \\ \Phi_{21} &= \mathbf{P}[(3d_{0a} 3d_{0a})1s_b'], \\ \Phi_{22} &= 2\mathbf{P}[(3d_{+1a} 3d_{-1a})1s_b'], \\ \Phi_{23} &= 2\mathbf{P}[(3d_{+2a} 3d_{-2a})1s_b'], \\ \Phi_{24} &= 2\mathbf{P}[(1s_a 3p_{0a})1s_b'], \\ \Phi_{25} &= 2\mathbf{P}[(1s_a 3d_{0a})1s_b'], \\ \Phi_{26} &= 2\mathbf{P}[(2s_a 3p_{0a})1s_b']. \end{aligned}$$

Potential Curve of the Metastable Helium Molecule*

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(Received 17 May 1963)

The potential curve of the He₂(³Σ_u⁺) molecule was computed using a twelve-term function containing orbitals through $3d$. The curve shows a potential maximum near $4.5 a_0$ which lies 0.081 eV above the calculated energy of the separated atoms. A similar maximum was obtained in two previous calculations which used a more restricted basis set. The maximum appears to be supported by experiment. In this calculation, $E_{\text{exp}}(\text{atoms}) - E_{\text{calc}}(r_e) = 0.94$ eV and $E_{\text{calc}}(\text{atoms}) - E_{\text{calc}}(r_e) = 1.24$ eV.

INTRODUCTION

THE potential curve of ³Σ_u⁺ He₂ (He₂^{*}) using simple one-configuration wave functions has been computed by Buckingham and Dalgarno¹ and Brigman, Brient, and Matsen.² Both calculations show a potential maximum near $4a_0$ (a_0 = first Bohr radius) which is a feature of considerable experimental interest. The present calculations extend the work of Brigman, Brient, and Matsen by adding polarization to the wave function. The calculations were performed using the CDC 1604 computer at the Computation Center at The University of Texas, and programs³ written by

members of the Molecular Physics Group at The University of Texas.

WAVE FUNCTIONS

The wave functions used in these calculations are constructed from Slater atomic orbitals. The ³Σ_u⁺ symmetry is achieved by forming bond functions⁴ from Slater determinants, and projecting the result with

$$\mathbf{P} = \frac{1}{4}(\mathbf{E} + \sigma_v)(\mathbf{E} - \mathbf{i}). \quad (1a)$$

Here \mathbf{E} is the identity transformation, σ_v is a reflection in a plane containing the molecular axis, and \mathbf{i} is an inversion through the center of the molecule.

The bond functions have the form

$$[(ab)cd] \equiv (ac:bd) + (bc:ad) + (ad:cb) + (bd:ca), \quad (1b)$$

where

$$(ab:cd) \equiv \det[a(1)\alpha(1)b(2)\alpha(2)c(3)\beta(3)d(4)\beta(4)]. \quad (1c)$$

⁴ H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1958).

* This research was supported in part by the Robert A. Welch Foundation of Houston, Texas, and the U. S. Air Force Office of Scientific Research, Contract AF-AFOSR-273-63.

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² G. H. Brigman, S. J. Brient, and F. A. Matsen, J. Chem. Phys. **34**, 958 (1961).

³ James Miller and J. C. Browne, *Collection Formulas for Diatomic Integrals* (Molecular Physics Group, 1962, The University of Texas, Austin, Texas).