

Thermal Emission of Electrons from Liquid Helium

W. SCHOEPE and G. W. RAYFIELD *

Physik-Department E 10 der Technischen Universität München, Germany

(Z. Naturforsch. **26 a**, 1392—1397 [1971]; received 29 June 1971)

The free surface of liquid helium acts as an energy barrier for electrons crossing the surface from the liquid into the vapor. The barrier is shown to be induced by the dielectric image-potential acting on the electrons below the liquid vapor interface. The application of an extracting electric field across the surface reduces the barrier and leads to a potential well below the surface which traps the electrons for extended periods of time. The escape into the vapor phase is shown to be dominated by thermal diffusion from the potential well according to Smoluchowski's equation. By measuring the escape rate a barrier height of 43.8 ± 0.7 K has been found. The top of the well lies 25 Å below the liquid vapor interface. Close to the λ -point and at higher temperatures the escape rate deviates from the theory. The relevancy of the present work for previous and further investigations of thermal electron emission from liquid helium is discussed.

1. Introduction

Electrons have proved to be a useful tool for the investigation of the excitations in superfluid helium, i. e. phonons, rotons, and quantized vortices. In the liquid the zero-point energy of a thermalized electron produces a bubble in which the electron is confined. These bubble states are usually called "negative ions". The transport of these electrons through the superfluid is governed by interactions with phonons, rotons and vortices¹. In the present work we have studied the escape of the electrons from the liquid through the free surface of liquid helium into the vapor phase.

CARERI, FASOLI, and GAETA² were the first who observed that electrons encounter increasing difficulty to pass through the free surface of liquid helium if the temperature is lowered. In a more detailed investigation, BRUSCHI, MARAVIGLIA, and MOSS³ measured the extracted current to be temperature independent from 4.2 K to 1.7 K. At lower temperatures, however, the current decreased rapidly according to $\exp\{-\Phi/T\}$, where Φ (25 ± 1 K) found to be independent of the extracting electric field varying from 20 V/cm to 200 V/cm. This behavior was mainly attributed to the image-force

acting on a charge near the interface of two media of different dielectric constants. The escape of the charge over the image-potential was described in a manner similar to thermionic emission of electrons from metals. The only differences to this analogue are given by the fact that the electronic density in the liquid is so low that Boltzmann statistics can be used and by the assumption that the image potential *inside* the liquid is relevant here. The branch outside can be neglected.

It can be readily shown⁴, that within this model the effective work function must depend on the electric field across the surface, in contrast to the results of Ref. ³. In addition the saturation of the currents at 1.7 K remained unexplained since this temperature is much smaller than the evaluated barrier Φ . In a more recent work⁵ the exponent Φ was found to depend on the electric field in agreement with the assumption of an image-force suggested in Ref. ³.

By treating the problem in terms of thermionic emission, all of this previous work^{3, 5} has neglected the small mean free path of the negative ions in the liquid. The image-potential in combination with an externally applied field leads to an energy well which traps the electrons below the surface for extended periods of time. The escape of the charges

Reprints request to Prof. G. W. RAYFIELD, Department of Physics, University of Oregon, Eugene, Oregon 97403, USA.

* Permanent address: Physics Department, University of Oregon, Eugene, Oregon, USA. ALFRED P. SLOAN fellow-supported in part by NSF Grant GP-13264.

¹ R. J. DONNELLY, *Experimental Superfluidity*, The University of Chicago Press, Chicago 1967.

² G. CARERI, U. FASOLI, and F. S. GAETA, *Nuovo Cim.* **15**, 774 [1960].

³ L. BRUSCHI, B. MARAVIGLIA, and F. E. MOSS, *Phys. Rev. Letters* **17**, 682 [1966].

⁴ Schottky effect, see e. g. C. HERRING and M. H. NICHOLS, *Rev. Mod. Phys.* **21**, 185 [1949].

⁵ W. SCHOEPE and C. PROBST, *Phys. Lett.* **31 A**, 490 [1970] and *Proceedings of the XII. Internat. Conf. on Low Temperature Physics*, Kyoto, to be published.

from the potential well into the vapor should be dominated by *thermal diffusion*. By measuring the trapping time of the negative ions in the well the actual barrier can be determined. Preliminary data were published recently in a short note⁶. An analysis of our results based on Smoluchowski's equation yields an image-potential induced energy barrier of 43.8 ± 0.7 K in zero electric field, the top of the well occurring 25 \AA below the surface. This implies that at the top of the well only 9 \AA of liquid exist between the bubble and the free surface of He II if a bubble radius of 16 \AA is assumed⁷. However, close to the λ -temperature and above the experimental results deviate from our theory. The reason for this behavior is not yet clear.

2. Measurement of the Trapping Time

The gold plated measuring cell (Fig. 1) consisted of a cylindrical copper bucket with three electrodes: the radioactive source S (^{241}Am having an activity of $23 \mu\text{Ci}$), a grid G, and the collector Co. The height of the liquid level was observed directly by means of a calibrated glass tube. The temperature was measured in-

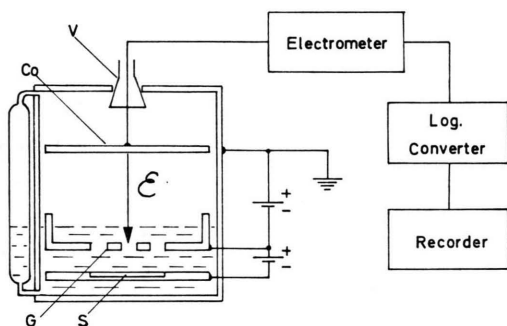


Fig. 1. Measuring cell and electronic set-up. S: radioactive source, G: grid, Co: collector, V: valve.

side the cell by a carbon resistor located at the bottom. The charges arriving at Co were measured by an operational amplifier (Keithley, Mod. 300) connected to a logarithmic converter (Moseley, 60 DM) and recorder (Moseley, 7100 BM). Helium was condensed into the cell after purification by a charcoal trap. The valve V was closed after the condensation, the liquid level being situated between G and Co. Data were taken by the following method. First the liquid surface was charged by suitable electric fields between S and Co. A guard ring at the grid potential prevents the surface charge from leaking to the walls of the cell. After a steady state is reached (i. e. the current arriving at Co

becomes time independent) the source current is switched off by means of grid G. The electric field \mathcal{E} across the liquid vapor interface is held constant. After a short transit time, the rate of charge escape from the surface into the vapor phase (I_s) is observed to decay exponentially with time $I_s(t) = I_s(0) \exp\{-t/\tau\}$, where τ is a constant for fixed electric field \mathcal{E} and temperature T (see Fig. 2). This implies that the number $\varrho(t)$ of the electrons at the surface decays exponentially be-

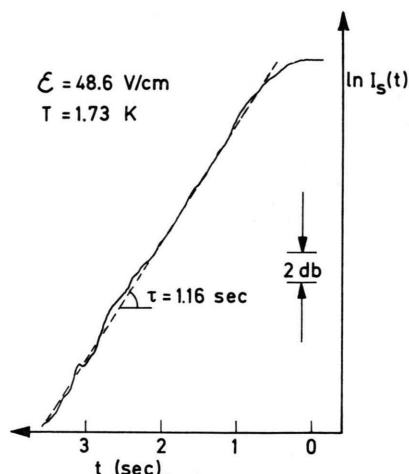


Fig. 2. Recorder diagram of a decaying current through the liquid surface.

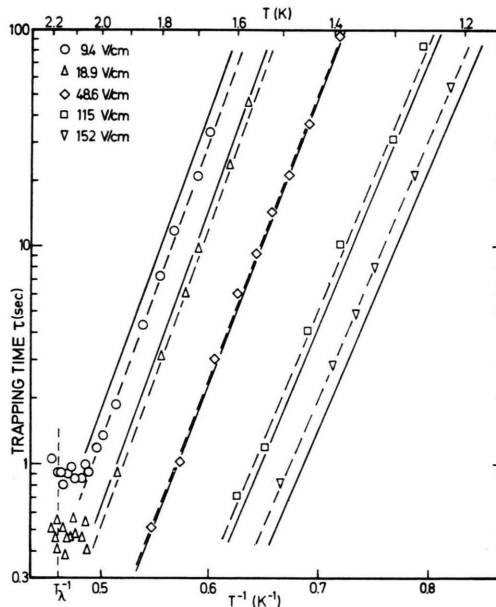


Fig. 3. Measured trapping times τ versus temperature for different electric field \mathcal{E} across the surface.

⁶ G. W. RAYFIELD and W. SCHOEPE, *Physics Letters* **31 A**, 133 [1971].

⁷ C. ZIPFEL and T. M. SANDERS, JR., *Proceedings of the XI. Internat. Conf. on Low Temperature Physics*, St. Andrews 1968, p. 296.

cause $q(t) = I_s(t) \cdot \tau$ where the time constant τ is the lifetime of the electrons at the surface (trapping time), and $1/\tau = P$ is the escape rate.

In Fig. 3 we have plotted the measured trapping times versus the temperature for five different electric fields \mathcal{E} . τ increases exponentially with decreasing temperature as can be seen from the straight line behavior in Fig. 3. There is a strong dependence of the τ values on the electric field \mathcal{E} . In addition also the slopes of the straight lines (dashed) depend on \mathcal{E} . We have observed trapping times ranging from 100 sec down to 0.4 sec. The upper limit is given by the fact that at low temperatures the steady state current $I_s(0)$ becomes small, and the lower limit for τ is determined by the risetime of the operational amplifier (≈ 0.2 sec) which could be neglected for τ values above 0.4 sec. Therefore, the region close to T_λ could be investigated only for the two lowest electric fields. Above 2.05 K the data deviate from the straight lines and show an appreciable scatter which extends above T_λ . In this region no further temperature dependence could be resolved. It should be mentioned that these τ data lie above the lowest τ values that could be measured accurately.

3. Discussion

We shall analyse the data in terms of an image-force model. The image-potential V_i inside the liquid is a hyperbolic function of the distance x of the electron from the surface (at $x=0$)

$$V_i(x) = \frac{e^2(\epsilon-1)}{4\epsilon(\epsilon+1)} \cdot \frac{1}{x} = \frac{A}{x}$$

where e is the electronic charge and ϵ the dielectric constant of liquid ^4He . If a homogeneous electric field \mathcal{E} is applied normal to the surface, the total potential is given by

$$V(x) = V_i(x) + e\mathcal{E}x = \frac{A}{x} + e\mathcal{E}x.$$

This potential has a minimum with a value of $2(Ae\mathcal{E})^{1/2}$ (Fig. 4). The barrier height seen by the electrons in the minimum is $\Phi_b - 2(Ae\mathcal{E})^{1/2}$ where Φ_b is a constant to be determined by experiment. The escape over the barrier should be dominated by thermal diffusion. Since the mean free path of the electrons in the well is small in the temperature range under investigation, the escape rate can be calculated from Smoluchowski's equation⁸. We get

$$P = 1/\tau = \left(\frac{V_A'' V_C''}{2\pi e} \right)^{1/2} \mu(T) \exp\left(\frac{\Phi_b - 2\sqrt{Ae\mathcal{E}}}{-T} \right) \text{sec}^{-1}.$$

⁸ H. A. KRAMERS, *Physica* **7**, 284 [1940], see also S. CHANDREASEKHAR, *Rev. Mod. Phys.* **15**, 63 [1943], Eq. (476).

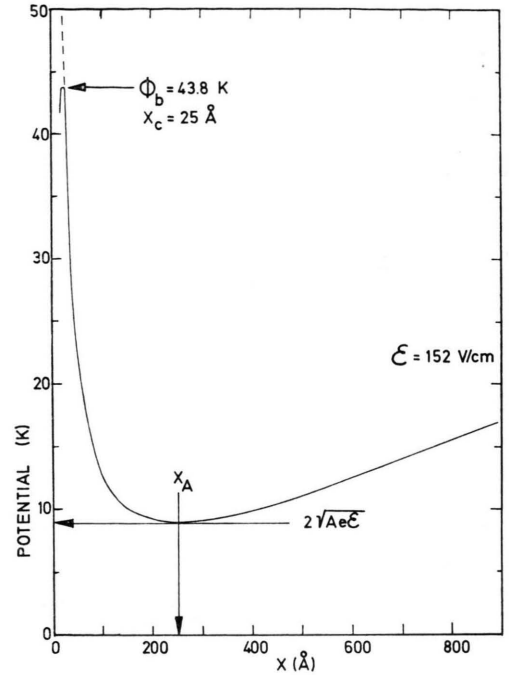


Fig. 4. The image-induced potential $V(x)$ near the surface of liquid ^4He is shown as a function of distance into the liquid.

Here, we have assumed a harmonic potential at the top of the well (at $x=x_c$) of the form

$$V(x) \approx \Phi_b - \frac{1}{2} V_c''(x-x_c)^2$$

and a harmonic potential at the minimum of the well (at $x=x_A$) of the form

$$V(x) \approx 2(Ae\mathcal{E})^{1/2} + \frac{1}{2} V_A''(x-x_A)^2.$$

The curvature V_c'' at the top of the well has to be determined from the experimental data. The curvature V_A'' at the minimum is calculated to

$$V_A'' = 2A(e\mathcal{E}/A)^{3/2}.$$

By numerical evaluation we have checked the harmonic approximation at the bottom of the well and have found it to be in agreement with an exact calculation to within few percent. $\mu(T)$ is the electron mobility⁹. Inserting the numerical values we get

$$1/\tau = 3.21 \cdot 10^7 \mathcal{E}^{3/4} (V_c'')^{1/2} \mu(T) \exp\left(\frac{\Phi_b - 0.72 \mathcal{E}^{1/2}}{-T} \right) \text{sec}^{-1} \quad (1)$$

where \mathcal{E} is measured in Volt/cm, Φ_b in K, and V_c'' in erg/cm². Φ_b and V_c'' depend on the physical process by which the electron escapes over the barrier

⁹ We take $\mu(T) = 1.2 \cdot 10^{-3} \exp(8.1/T)$ cm²/Vsec; see W. P. PRATT, JR., and W. ZIMMERMANN, JR., *Phys. Rev.* **177**, 423 [1969].

at $x = x_c$ and are determined from a best fit to the experimentally measured values of τ . From the measured five curves we obtain:

$$\begin{aligned}\Phi_b &= 43.8 \pm 0.7 \text{ K}, \\ V_c'' &= (3.10 \pm 1.76) \cdot 10^3 \text{ erg/cm}^2.\end{aligned}$$

Equation (1) is plotted in Fig. 3 (full lines) with $\Phi_b = 43.8 \text{ K}$ and $V_c'' = 3.10 \cdot 10^3 \text{ erg/cm}^2$ ($2.25 \cdot 10^3 \text{ K/\AA}$). While $\Phi_b = 43.8 \text{ K}$ is an excellent fit to the temperature dependence of the data, the absolute values of τ are in better agreement if the $\mathcal{E}^{3/4}$ dependence is changed to an $\mathcal{E}^{0.5}$ dependence (dashed lines). At the moment we have no explanation for this slightly different value in the power of \mathcal{E} . It might be caused by a field dependence of the curvature at the top of the barrier which is not taken into account in our harmonic approximation. It should be noted that the value found for V_c'' is extremely large, i. e. the curvature is very sharp. (Within the harmonic approximation, the potential drops to zero within 0.3 \AA .) At the top of the well, with a bubble radius of 16 \AA , only 9 \AA of liquid exist between the wall of the bubble and the surface of the liquid. Therefore the electron might escape quite easily by other mechanisms than by diffusion, e. g. by tunneling. Then the problem is treated by assigning an effective curvature to the barrier. These processes would be consistent with the large value of V_c'' which is found.

Earlier observations indicate that positive ion currents through the free surface are very small compared to electron currents³. Within the framework of our model this means that Φ_b should be larger and/or V_c'' much smaller than in the present case. A detailed investigation of the positive charges would be desirable¹⁰.

The temperature region close to T_λ deserves a special discussion. The electron mobility $\mu(T)$ changes continuously from an exponential behavior below T_λ to a nearly temperature independent value above T_λ . Hence, the exponent in the temperature dependence of τ should increase by 8.1 K . From Fig. 3, however, it is obvious that above 2.05 K the data lie above the theoretical curve and show an appreciable scatter. This behavior extends into the normal

fluid regime. The scatter is caused by the experimental resolution in this regime: The current is observed to decay exponentially only after having decreased to a low value. (After switching off the source, the current remains stable depending on the time required for the charges to move from the grid to the surface. Then the current starts decaying. Only after a transition time has elapsed, which is greater than the trapping time, the decay exhibits an exponential behavior. Only this final portion of the decay could be used to determine the trapping time in this temperature regime.) The deviation of the data from the extrapolated straight line behavior, however, remains unclear^{10a}. Further experimental work with better time resolution seems to be necessary to decide whether this deviation is related to the superfluid phase transition itself. Our theoretical model, which leads to Eq. (1) should be applicable for both normal and superfluid region.

4. Implications to Previous Work

Now we are able to understand at least qualitatively the previous^{3,5} results on the temperature dependence of the steady state emission current. At higher temperatures the trapping time at the surface is short enough to have no effect on the transport of electrons across the surface. The emitted current is identical to the current measured with the liquid level raised above the collector. With decreasing temperature, however, the trapping times increase rapidly. The current arriving at the liquid surface splits into two components: part of the charges diffuse over the surface barrier into the vapor phase, the rest leaking to the walls of the measuring cell. This process could occur quite easily since no guard ring prevented the charges from flowing in the potential minimum to the grounded walls⁵. When the trapping time has become comparable to the transit time to the walls the current will begin to decrease with decreasing temperature (see Fig. 5). But this decrease need not resemble the temperature dependence of the trapping time. The emitted current is given by the number ϱ of the charges in the potential well times the escape rate $P = 1/\tau$:

$$I_s(T, \mathcal{E}) = P(T, \mathcal{E}) \varrho(T, \mathcal{E}).$$

¹⁰ Preliminary tests with positive ions were performed by the authors together with F. WAGNER. The experiments, however, were seriously disturbed by a strong emission of electrons from the collector simulating a positive current. This effect was found not to be caused by the gamma radiation

of the radioactive source itself. A superfluid film on the collector reduced the emission of these electrons.

^{10a} The mobility change near T_λ from the exponential behavior is unable to account for this deviation.

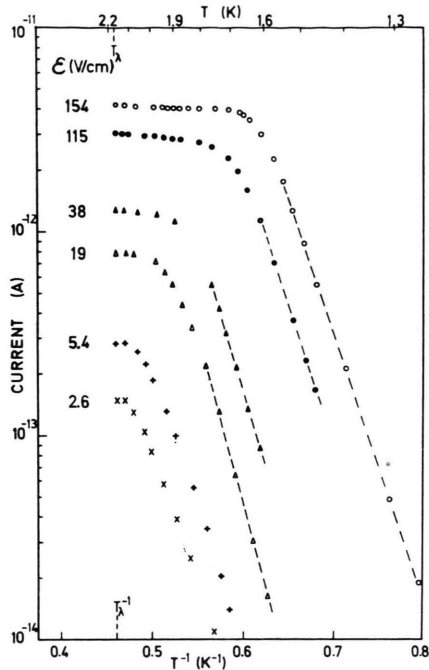


Fig. 5. Steady state emission current from the surface versus temperature for different extracting fields \mathcal{E} (from Ref. ⁵).

From the known escape rate and the measured currents ρ can be calculated. This is shown in Fig. 6 for two representative curves of Fig. 5. With decreasing temperature ρ first increases due to the increasing trapping time. At lower temperatures when nearly all charges are leaking to the walls, ρ begins to decrease because of the increasing mobility to the wall. From Fig. 6 it can be seen that in this region ρ decreases proportional to $\exp\{-4/T\}$. This may be understood by assuming that the current I to the walls (one dimensional) is space charge limited and roughly temperature independent, giving

$$I = \rho \mu \mathcal{E}_{\parallel} \propto \rho \mu \sqrt{I/\mu},$$

$$\text{whence } \rho \propto \sqrt{I/\mu} \propto \exp\{-4/T\},$$

where \mathcal{E}_{\parallel} is the electric field parallel to the surface. This result justifies our earlier assumption [Eq. (1)] using the bulk mobility, thereby neglecting any possible contribution of surface excitations. In summary, it is obvious that the actual surface barrier cannot be deduced from these steady state measurements. The observation that at low electric fields the

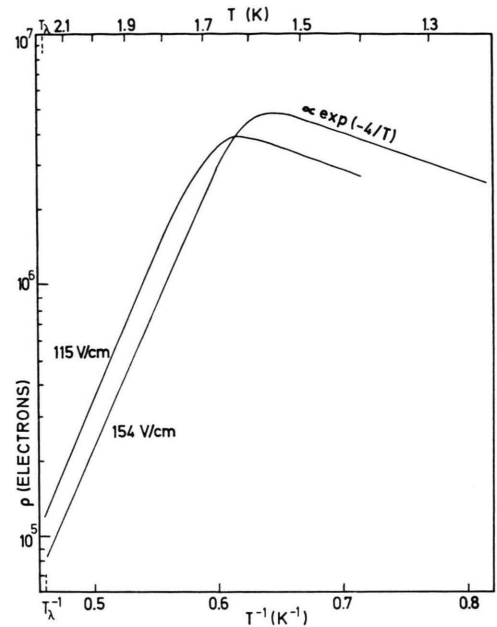


Fig. 6. Number ρ of electrons in the potential well below the surface for two curves of Fig. 5 calculated from the escape rate P .

onset of the current drop approaches T_{λ} (see Fig. 5) may now be considered as a combination of a geometry effect and the observation that below 2.05 K the trapping times increase rapidly.

5. Further Comments

Calculations by COLE and COHEN¹¹ postulate the existence of image-potential induced surface states for electrons just above the liquid surface. These states have been recently observed by WILLIAMS et al.¹² Since the lifetime of the electrons in these states is of the order of 10^{-4} sec¹², in our experiment these states outside the liquid can be neglected. In Ref. ¹² few preliminary results of the trapping time inside the liquid are presented. Although the experimental error is rather large, the data seem to be in good agreement with the results presented in this paper.

There are several steady state experiments on electron emission from liquid helium which should be repeated with the present method: 1. Emission from the free surface of liquid ^3He and $^3\text{He}-^4\text{He}$ mixtures⁵; 2. Electron transport through the $^3\text{He}-$

¹¹ M. W. COLE and M. H. COHEN, Phys. Rev. Letters **23**, 1238 [1969].

¹² R. WILLIAMS, R. S. CRANDALL, and A. H. WILLIS, Phys. Rev. Letters **26**, 7 [1971].

4He phase boundary¹³; 3. Emission of electrons trapped in vortex lines of rotating superfluid helium¹⁴. These experiments are presently being performed. A comparison of the results for the barriers Φ_b and their curvatures V_c'' would be quite interesting, since these quantities are determined by mechanisms taking place few Ångström below the surface. Such further work should also throw some light on the physical process by which the electrons escape from the bubble state into the vapor phase. The full extent to which this method can be used to study the free surfaces of dielectric liquids, however, is not yet obvious.

Acknowledgements

We acknowledge the contribution of C. PROBST to part of the steady state measurements. We also thank K. DRANSFELD, H. SCHMIDT, and D. STAUFFER for valuable discussions, and the Zentralinstitut für Tief-temperaturforschung der Bayerischen Akademie der Wissenschaften for their hospitality. The Deutsche Forschungsgemeinschaft supported this work and a visit to München by one of us (G. W. R.).

¹³ M. KUCHNIR, P. R. ROACH, and J. B. KETTERSON, J. Low Temp. Phys. **3**, 183 [1970].

¹⁴ W. SCHOEPE and K. DRANSFELD, Phys. Letters **29 A**, 165 [1969].

Quantenchemische Untersuchungen an Acetylen, Tetrachloroaluminat(III)-ion und Lithiumtetrachloroaluminat(III)

P. DROSSBACH

Physikalisch-chemisches und elektrochemisches Institut der Technischen Universität München

und H. HOFF

Max-Planck-Institut für Metallforschung, Institut für Metallkunde

(Z. Naturforsch. **26 a**, 1397—1406 [1971]; eingegangen am 31. März 1971)

Die Moleküle bzw. Ionen C_2H_2 , $AlCl_4^-$ und $LiAlCl_4$ wurden unter Berücksichtigung aller ihrer Elektronen nach dem SCF-MO-LC-LCGO-Verfahren berechnet. Orbitalenergien, Besetzungsarten, Orbitalschwerpunkte und Dipolmomente wurden mitgeteilt. Die Röntgen-Terme werden im Vergleich zu den freien Atomen durch die chemische Bindung in den Molekülen nicht nur abgesenkt, sondern können durch die Elektronenwechselwirkung auch angehoben werden. Die Entladung eines Ions bei gleichzeitigem Übergang mehrerer Elektronen wird diskutiert.

1. Das Acetylenmolekül

In früheren Arbeiten¹ wurde zur Charakterisierung der Bindungsverhältnisse in einigen Molekülen zusätzlich zu den Orbitalenergien und Elektronendichten auch die Lage der Orbitalschwerpunkte herangezogen. Von Interesse war es, nun zu untersuchen, wie bei symmetrischen Molekülen mit dem Dipolmoment null die Schwerpunkte der einzelnen Orbitale sich so zusammensetzen, daß der Gesamtschwerpunkt von Kernen und Elektronen zusammenfällt. Es wurde daher die von PREUSS und Mitarbeitern² schon durchgeführte Rechnung des Acetylens jetzt unter zusätzlicher Berechnung der Orbitalschwerpunkte wiederholt.

Die Resultate sind in der folgenden Tab. 1 mitgeteilt. Die Besetzungsarten mit *s*- bzw. *p*-Funk-

tionen wurden in der in der Chemie üblichen Weise bildlich dargestellt. Die Koordinaten auf der *z*-Achse waren:

Kern	H ₁	H ₂	C ₁	C ₂
<i>z</i> -Koordinate	— 2,100	4,407	0,0	2,307

Gerechnet wurde mit je 3 Gauß-Funktionen für die H-Atome, je 5 für die C-Atome und 16 Gauß-Gruppen zur Beschreibung der *p*-Funktionen.

Die Schwerpunkte der Orbitale 3 bis 6 fallen genau in das Symmetriezentrum des Moleküls. Die Schwerpunkte der Orbitale 1 und 2 liegen links bzw. rechts vom Symmetriezentrum; beide zusammen vereinigen sich jedoch im Symmetriezentrum. Dieser Tatsache, daß bei symmetrischen Molekülen oder Ionen die Schwerpunkte zweier oder mehrerer

¹ P. DROSSBACH u. P. SCHMITTINGER, Z. Naturforsch. **25 a**, 833, 834, 1269 [1970].

² Arbeitsbericht der Gruppe Quantenchemie, Max-Planck-Institut f. Phys. u. Astrophys., München, Nr. 5.