PHYSICAL REVIEW B VOLUME 45, NUMBER 7 15 FEBRUARY 1992-I

Pressure dependence of the conduction-band energy of nonpolar liquids

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(Received 17 September 1991)

The energy V_0 of the conduction state of the quasifree electron is reported as a function of pressure up to 2.5 kbar for *n*-pentane, 2,2-dimethylbutane, 2,2,4-trimethylpentane, 2,2,4,4-tetramethylpentane, and tetramethylsilane (TMS). For each liquid, V_0 increases with increasing pressure. The largest change with pressure is observed for *n*-pentane, the smallest change for TMS. The results are used together with a density-fluctuation theory to calculate the effect of pressure on the mobility of quasifree electrons. The theory predicts the direction of change in mobility with pressure found experimentally (decreasing with pressure for TMS and increasing with pressure for branched hydrocarbons) as well as the relative magnitude of the changes.

I. INTRODUCTION

The energy of the conduction band for many nonpolar liquids has been measured under a variety of conditions.[1] Several studies have shown how the energy of the bottom of the conduction band, V_0, varies with density.[2] In general, it is found that V_0 decreases from zero with increasing density, passes through a minimum, and then, at densities near the normal liquid density, increases with density. Such studies have been done either by varying the temperature or by varying the concentration isothermally above the critical temperature. However, little information is available on precisely how V_0 changes at higher densities; that is, above the normal liquid density. One study[3] on nonpolar molecular liquids reported V_0 data for temperatures below room temperature and those data indicate that V_0 increases at higher densities.

The present study was done to determine how V_0 changes with increasing density by applying static pressures to 3 kbar to various liquids. It was motivated by our other studies of mobility[4,5] and electron reactions[6] at high pressure. The quantity V_0 and, in particular, its derivative dV_0/dN (where N is the number density), are important parameters in theories of electron mobility, and electron reactions are dependent on V_0 as well. Thus it is important to the interpretation of such studies to know how pressure affects the energy of the bottom of the conduction band.

The experiments reported here involve measuring the current from a liquid-filled photocell placed inside a pressure vessel that is equipped with a window for the monochromatic light beam to enter. The work function (Φ) of the photocathode, which is determined from the wavelength response of the measured photocurrent, is measured as a function of pressure. Changes in Φ with pressure are interpreted as changes in the conduction-band energy V_0 with pressure.

II. EXPERIMENT

A. Photocell

The photocell employed is shown schematically in Fig. 1. The bellows allows for volume changes on pressurization. The two electrical feedthroughs are for (i) negative high voltage, supplied to the photocathode from a Bertran Associates model 305 supply, and (ii) for photocurrent, measured on the grid. Light enters the cell through the sapphire window at the bottom. This sapphire window proved useful to 2.5 kbar; above that pressure rupture occurred. The photocathode (*C*) is coated with Zn by vapor deposition from a W-filament heater in a separate bulb on a vacuum line; after coating it is transferred to the photocell. The lower miniconflat flange is opened for this purpose. The transfer is done in a N_2-filled glove bag to minimize exposure of the cathode to oxygen.

B. Liquids

The 2,2-dimethylbutane and 2,2,4-trimethylpentane were Wiley 99.9% grade. The 2,2,4,4-tetramethylpentane was Wiley calorimetry grade. The tetramethylsilane was Aldrich 99.9+%. The *n*-pentane was Wiley 99% pure. These liquids were further purified by the same procedure[5] used to prepare samples for drift-mobility studies. This involved drying with silica gel, degassing on a vacuum line, passage through a high-purity silica gel and molecular-sieve column, and final storage over NaK. The *n*-pentane was also precleaned by several washes with H_2SO_4 followed by several washes with deionized water. After purification the liquid samples are distilled into the photocell, while the cell is cooled to −60 °C.

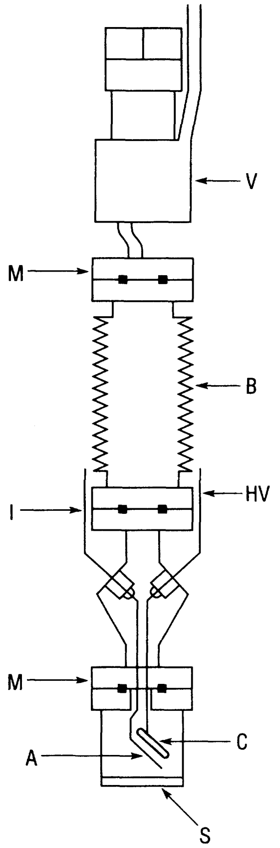

FIG. 1. Schematic of sample cell. *V*, valve; *M*, custom miniconflat flange; *B*, stainless-steel bellows; *I*, current lead; HV, high-voltage lead; *C*, Zn photocathode; *A*, 90%-transparent Ni mesh grid; *S*, sapphire window.

C. Pressure vessel

The cell containing the liquid sample is placed inside the pressure vessel, built by the Leco Corp.'s Tem-Press Division. This vessel is fitted with a 0.75-in.-thick sapphire window at one end that permits light to enter, as well as holding high pressures. The closure at the other end contains high-pressure, high-voltage feedthroughs (Alberox) for electrical connections.

D. Light source

The light source is a 200-W xenon lamp (Oriel). A 20-mm-focal-length monochromator (Instruments SA, model H20) with a holographic grating provides monochromatic light. Although stray-light rejection is excellent with this monochromator, filters are also used to eliminate light of shorter wavelengths. A photodiode (Hamamatsu S1337-1010BQ) of known spectral response characteristics serves as a monitor of light intensity.

E. Data acquisition

Software was developed to control the experiment and to acquire data using an IBM PS/2 model 60 computer. At each wavelength the photocurrent is measured with a Kiethley 610BR picoammeter. The output voltage of the picoammeter is sampled many times at each wavelength with a computer interface (Stanford Research Systems SR245). This unit also measures the voltage output of the photodiode monitoring the light intensity. Both voltage signals are transferred to the computer through a GPIB interface. The digital ports of the SR245 are used to output transistor-transistor logic (TTL) pulses in order to change the wavelength of the monochromator automatically through a stepping motor. Repetition of this process generates a table of photocurrent (*i*) and light intensity (*I*) as a function of wavelength. Measurements are made at room temperature, 22±1 °C. After each pressure change adequate time (approximately 15 min) is allowed for temperature equilibration of the liquid prior to data acquisition.

F. Data analysis

The photocurrent data as a function of wavelength are fitted to the Fowler function $F(x)$, where x is $(h\nu\text{-}\Phi)/k_BT$, to determine the work function. In this method the photoelectric yield (Y) in electrons per photon is given by

$$Y = aAT^2F(x) \ , \tag{1}$$

where A is a universal constant and a is the fraction of electrons that absorb a photon and escape the metal. For positive x, $F(x)$ is given by

$$F(x) = x^2/2 + \pi^2/2 - \exp(-x) + \tfrac{1}{4}\exp(-2x) - \tfrac{1}{9}\exp(-3x) + \cdots \ . \tag{2}$$

A plot of the data in the form $\log_{10}(Y/T^2)$ versus x is fitted to Fowler's function by a nonlinear-least-squares program.[7] The work function (Φ) is determined by the shift parallel to the x axis. This method gives a satisfactory fit to the data for liquids at photon energies up to 0.5 eV above the work function.[3,8]

III. RESULTS

To determine the effect of pressure, the photoelectric response is first measured at 1 bar with the liquid in the

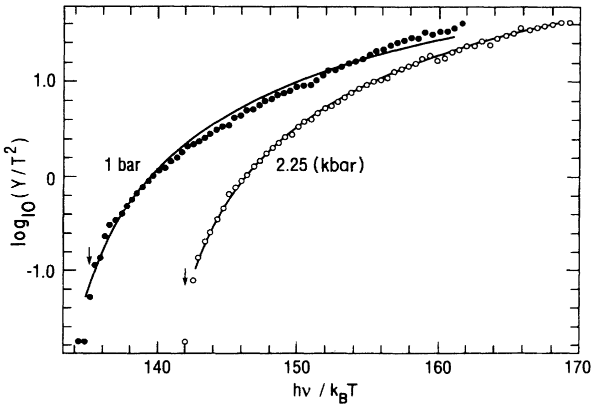

FIG. 2. Response of photocell filled with 2,2,4-trimethylpentane at 1 bar and 2.25 kbar. Lines correspond to Fowler-function fits. Arrows indicate work-function shift; ΔV_0 is 0.177 eV in this case.

cell. The cell is then pressurized and the response remeasured. Finally, the experiment is repeated at 1 bar. Examples of such data for 2,2,4-trimethylpentane are shown in Fig. 2 along with a least-squares fit of the data to the Fowler function. The results for other liquids were similar. The currents measured were generally between 10^{-14} and 2×10^{-11} A. For *n*-pentane the maximum currents observed were around 3×10^{-12} A. The currents are very small in the vicinity of the work function; therefore, to minimize errors due to random noise, several spectral scans were made at each pressure. The errors on each data set are about ±0.01 eV.

In every liquid the work function increases with increasing pressure, but the rate of change of Φ with pressure is dependent on the liquid. The difference in work functions,

$$\Delta V_0 = \Phi_P - \Phi_1 , \tag{3}$$

is denoted ΔV_0, where Φ_1 is the average value of the work function at 1 bar measured before and after pressurization.

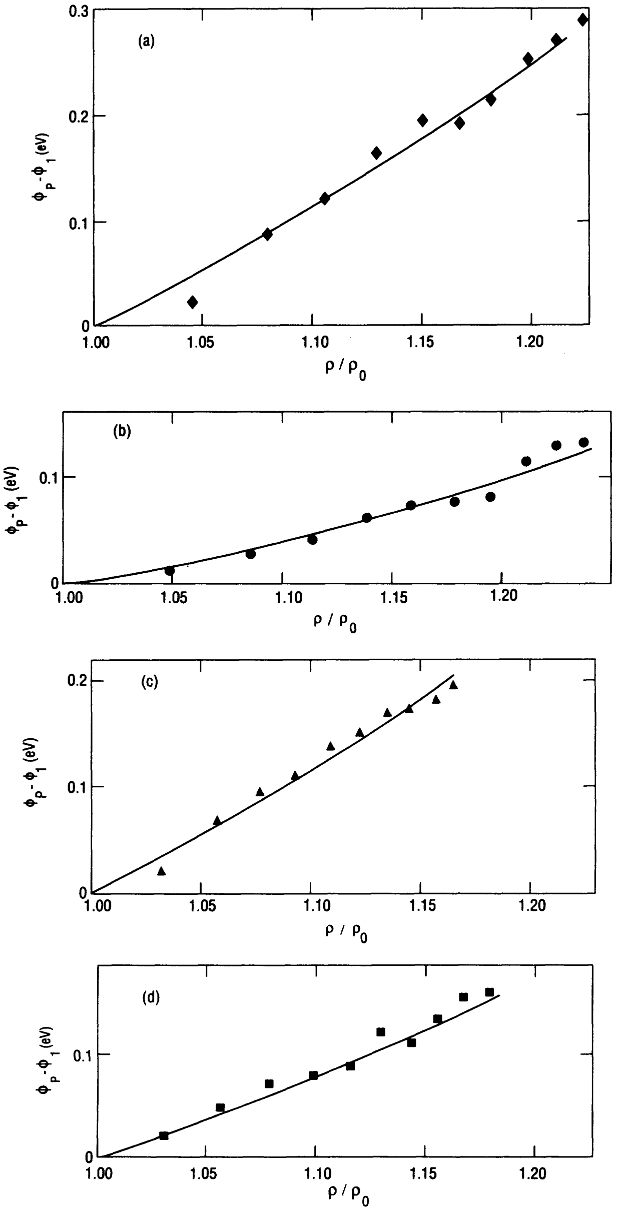

FIG. 3. Change in work function, ΔV_0, as a function of density for (a) *n*-pentane; (b) tetramethylsilane; (c) 2,2,4-trimethylpentane; (d) 2,2-dimethylbutane.

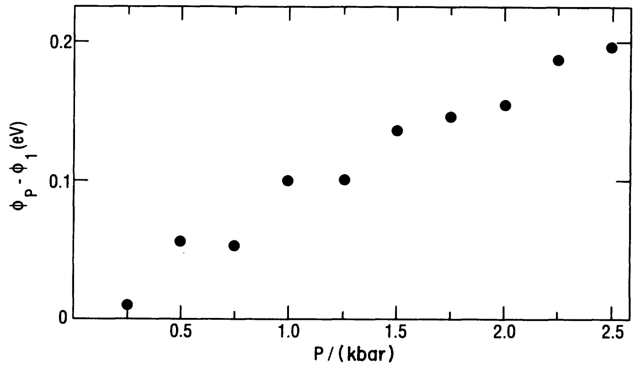

FIG. 4. Change in work function, ΔV_0, as a function of pressure for 2,2,4,4-tetramethylpentane.

Five liquids were studied which represent different molecular structures and different absolute values of V_0. At 298 K and 1 bar for *n*-pentane, a straight-chain alkane, V_0 is 0.0 eV; for tetramethylsilane, a symmetrical molecule, V_0 is quite low, −0.56 eV. Three branched-chain alkanes were studied that have intermediate values of V_0 at 1 bar. The observed shifts with pressure, ΔV_0, for each liquid are shown in Figs. 3(a)–3(d). In each case the total pressure range is from 1 bar to 2.5 kbar. For *n*-pentane, the maximum ΔV_0 observed is nearly 0.3 eV [Fig. 3(a)], while for TMS the change is 0.13 eV [Fig. 3(b)]. The results for 2,2,4,4-tetramethylpentane are shown plotted versus pressure (Fig. 4) because the density as a function of pressure is not known. The V_0 data obtained at low temperatures[3] are very limited, there being only a few points for each liquid. Nevertheless, the low-temperature data[3] are in qualitative accord with the results in Fig. 3.

IV. DISCUSSION

The work-function shifts observed are attributed to changes in the conduction-band energy of the liquid. This interpretation is only valid if the energy levels of the metal either do not change, or change by a negligible amount, for the pressures applied. That the Fermi energy of metals, and Zn in particular, does not change significantly for the pressures employed may be inferred in several ways. First, metals are much less compressible than liquids. The compressibility of Zn is anisotropic,[9] but, even assuming its maximum value, the volume contracts only 0.3% at 2.5 kbar. The resistivity of Zn decreases smoothly with increasing pressure; the decrease is only 1% at 2.5 kbar. There are no sharp discontinuities indicative of a phase transition over this pressure range[10] that could alter the Fermi level. A theoretical estimate of the shift in the Fermi level may be made using the Wigner-Seitz model. According to Knopoff,[11] the Fermi energy is given (in Rydbergs) by

$$F_e = 2.21\alpha / r_0^2 \ , \tag{4}$$

where α is the effective number of free electrons per atom and r_0 is the Wigner-Seitz radius in Bohrs. From Eq. (4) and the measured compressibility, the Fermi level of Zn would change by +0.015 eV when the pressure increases from 1 to 2500 bars. However, this is an overestimate since the maximum value of the compressibility of Zn was used. This change in the Fermi level is negligible compared to the observed work-function shifts. Our assumption is therefore justified that observed changes in work function may be associated with changes in the conduction-band energy of the liquid.

As shown in Figs. 3 and 4, V_0 increases as the pressure increases; the largest change is observed in each case at the maximum pressure applied, which in this study is 2.5 kbar. Table I summarizes the data at 1 bar and 2.5 kbar for four of the liquids. The observed increases in V_0 over this pressure range for n-pentane, tetramethylsilane (TMS), 2,2-dimethylbutane, 2,2,4-trimethylpentane, and 2,2,4,4-tetramethylpentane are 0.29, 0.13, 0.15, 0.20, and 0.19 eV, respectively. The earlier measurements of V_0 at low temperatures[3] are in qualitative agreement with the present results.

The Springett-Jortner-Cohen (SJC) model[12] predicts that V_0 should increase with increasing density. In this model, V_0 is the sum of the polarization potential U_p and the kinetic-energy term $T_0 = \hbar k_0^2/2m$; thus, $V_0 = U_p + T_0$, where k_0 must satisfy the Wigner-Seitz boundary condition: $\tan[k_0(r_s - \tilde{a})] = k_0 r_s$. The radius r_s is given by $(3/4\pi N)^{1/3}$, $\tilde{a}$ is a hard-core radius parameter, and N is the number density. This model has recently been used together with a high-precision pseudopotential and shown to give excellent agreement with experimental data for liquid rare gases and methane.[13] We used the original model and experimental values of V_0 at 1 bar first to evaluate $\tilde{a}$ and then use it to predict how V_0 should change with density. The values of $\tilde{a}$ found here are in reasonable agreement with those reported in an earlier study.[3] In each case we find that this theory predicts a greater increase in V_0 with pressure, by 30–60 %, than is observed experimentally (compare columns 4 and 6 of Table I). The data thus are not very well represented by this model. If we instead use the SJC model to calculate the hard-core radius at each density from the observed V_0 values, then $\tilde{a}$ decreases slightly, about 1% over 2.5 kbar (see column 8 of Table I).

For the purposes of both representing the V_0-versus-density data and obtaining the derivative dV_0/dN, the data were fitted to an analytic equation. Since V_0 reaches a minimum value, $V_0(\min)$, at some lower density, $N(\min)$, the data can be represented by a parabola:[14]

$$V_0 = V_0(\min) + [N - N(\min)]^2/B \ . \tag{5}$$

In the case of n-pentane and TMS, V_0 data are available in the region of the minimum. For TMS,[15] $V_0(\min)$ is -0.61 eV and $N(\min)$ is 3.39×10^{21} cm^{-3}; for n-pentane,[2] $V_0(\min)$ is -0.28 eV and $N(\min)$ is 2.4×10^{21} cm^{-3}. We find from our results that the values of B are 24.8×10^{42} for TMS and 26.9×10^{42} for n-pentane. For the other hydrocarbons there are no experimental values of V_0 available near the minimum. For these the SJC model was used to find the value of $V_0(\min)$ and then the data were least-squares-fitted to Eq. (5) to find $N(\min)$ and B. We find, for 2,2-dimethylbutane, $V_0(\min) = -0.39$ eV, $N(\min) = 2.78 \times 10^{21}$, and $B = 23.6 \times 10^{42}$, and, for 2,2,4-trimethylpentane, $V_0(\min) = -0.39$ eV, $N(\min) = 2.5 \times 10^{21}$, and $B = 8.45 \times 10^{42}$. Values of V_0 and dV_0/dN in Table I are calculated from Eq. (5) and these parameters.

Although an earlier study[16] associated V_0 with the heat of solution of the electron, Hamill[17] later suggested that V_0 is the free energy for transfer of the electron from the vacuum to the quasifree state in the liquid. It follows from this suggestion that the change in V_0 with pressure,

TABLE I. Conduction-band energies at 22 °C. Values in parentheses are assumed.

Liquid	Pressure (bars)	N (10^{21} cm^{-3})	V_0 (eV) Expt.	V_0 (eV) Calc. Eq. (5)	V_0 (eV) Calc. SJC	dV_0/dN (10^{-34} ergs cm^3)	$\tilde{a}$ (Å)
n-pentane	1	5.19	0.0[a]	−0.001	(0.0)	3.21	2.029
	2500	6.35	0.29	0.28	0.46	4.58	2.002
TMS	1	4.39	−0.56[b]	−0.56	(−0.56)	1.29	2.065
	2500	5.43	−0.43	−0.44	−0.39	2.63	2.056
2,2-DMB	1	4.51	−0.26	−0.26	(−0.26)	2.35	2.105
	2500	5.35	−0.11	−0.11	−0.01	3.48	2.089
2,2,4-TMP	1	3.63	−0.24[c]	−0.24	(−0.24)	4.28	2.342
	2500	4.23	−0.045	−0.036	+0.01	6.55	2.333

[a] Reference 1.

[b] Reference 14.

[c] Reference 3.

or dV_0/dP, is then ΔV_s, the volume change for solution of the electron; that is, the partial molal volume of the electron. The value of dV_0/dN can be calculated from the derivative of Eq. (5) and ΔV_s can be evaluated from

$$\Delta V_s = \frac{dV_0}{dP} = \frac{dV_0}{dN} N \chi_T Z \ , \tag{6}$$

where χ_T is the isothermal compressibility and Z is Avogadro's number. This analysis gives 50 cm^3/mol for TMS at 1 kbar. For other liquids larger values (e.g., 136 cm^3/mol for 2,2,4-TMP at 1 bar) are obtained from Eq. (6) because of the larger values of dV_0/dN. These large positive values of the volume of the electron rest on the validity of Hamill's assumption. We do not necessarily agree that V_0 is exactly equivalent to the free energy of solution of an electron, but if the former term increases with pressure, then the latter one is likely to do so. That is, the energetics change because the electron, while in an extended state, is confined to less space at higher densities. The origin of this energy change is primarily the repulsive part of the electron-molecule forces. It is quite conceivable that this may give rise to an increased volume on solution of an electron. Theoretical models[12,13] of quasifree electrons in liquids have assumed no volume change.

Mobility calculations

Current theories of quasifree mobility of electrons depend on the value of the derivative of V_0 since scattering is assumed to arise from fluctuations in potential due to density fluctuations. These theories lead to an equation for the drift mobility of the form

$$\mu_F = (2e/3)(2/\pi m^* k_B T)^{1/2} \Lambda \ , \tag{7}$$

where

$$\Lambda = C\hbar^4/(m^*)^2 N^2 k_B T \chi_T (V_0')^2 \ , \tag{8}$$

e is the electronic charge, m^* is the effective mass of the electron, and k_B is Boltzmann's constant. The constant C is $36/\pi$ in the theory of Berlin, Nyikos, and Schiller[18] and is equal to π in the theory of Basak and Cohen.[19] The latter theory leads to a similar expression if higher-order derivatives of V_0 are neglected. The value of C assumed here is π. With the present data all parameters in Eq. (7) are known if m^* is taken equal to the electron mass and μ_F can be evaluated.

TMS is a liquid in which the electron is quasifree.[20] The experimental drift mobility in TMS decreases as the pressure increases (column 7 of Table II); the decrease is about 15% at 25 °C. Calculated values of μ_F from Eq. (7) also show a decrease with increasing pressure (column 6 of Table II). The relative decrease in μ_F is comparable to that observed experimentally.

2,2-dimethylbutane is also a liquid for which Hall-mobility experiments indicate that the electron is quasifree.[21] Thus a comparison of observed drift-mobility data with the predictions of Eq. (7) are of interest and are shown in the last two columns of Table II. The theory predicts that μ_F should increase with pressure by 70% at 23 °C, and this compares reasonably well with the observed increase of 30%.

A similar increase in μ_F (of 40%) is predicted for 2,2,4-trimethylpentane at 23 °C and this is very close to the observed increase[14] of 38%. Although electrons are trapped at least part of the time in this liquid, it was

TABLE II. Mobility calculations.

Temperature (°C)	Pressure (bars)	N (10^{21} cm^{-3})	χ_T (10^{-10} cm^2/dyn)	V_0' (10^{-34} ergs cm^3)	μ_F (cm^2/V s) Calc.	Expt.[a]
			Tetramethylsilane			
25	1	4.37	2.53	1.29	197.0	102.0
	2500	5.43	0.42	2.64	183.0	85.0
50	50	4.33	2.60	1.213	195.0	104.0
	2500	5.38	0.428	2.573	171.0	78.0
100	50	3.85	5.92	0.594	364.0	111.0
	1000	4.70	1.019	1.689	176.0	75.0
			2,2,-dimethylbutane			
23	1	4.51	1.782	2.35	80.0	11.0
	2500	5.35	0.339	3.48	136.0	14.0
60	1	4.26	2.802	2.01	65.0	13.4
	2500	5.26	0.375	3.36	114.0	13.6
100	1	4.06	4.091	1.74	55.0	17.0
	2500	5.20	0.420	3.28	92.0	13.5
			2,2,4-trimethylpentane			
23	1	3.63	1.454	4.28	46.0	
	2500	4.23	0.322	6.55	65.0	
			n-pentane			
23	1	5.19	2.241	3.21	26.0	
	2500	6.35	0.397	4.58	48.0	

[a] μ_{expt} from Refs. 4 and 13.

shown earlier that changes in the mobility are dominated by changes in μ_F.[22] The lower mobility then can be attributed to the effect of the traps.

The theory thus predicts the direction of change of the mobility with pressure and the relative magnitude of change. However, there are some points of disagreement between theory and experiment. In the case of TMS the theory overestimates the observed mobility by a factor of about 2. In the case of 2,2-dimethylbutane this factor is even larger. Also, for this liquid an increase in μ_F as pressure increases is also predicted at higher temperatures, whereas experimentally the mobility is nearly independent of pressure at 60 °C and decreases with increasing pressure at 100 °C.

An increase in μ_F with pressure is also predicted for *n*-pentane. (In this case there are no experimental values available for comparison.) It seems that such an increase will usually be predicted by this theory largely due to the decrease in the isothermal compressibility with pressure; at 2.5 kbar χ_T is typically about $\frac{1}{5}$ of its value at 1 bar. In the alkanes the other variables, V_0' and N, do not change so much with pressure. However, in the case of TMS a much larger change in V_0' occurs over this pressure range, and since the mobility depends on the square of this variable, the increase in V_0' nearly compensates for the decrease in compressibility and, therefore, as N increases, a slight decrease in μ_F is predicted.

ACKNOWLEDGMENTS

The authors thank F. Holroyd for his comments on the Fermi energy. This research was carried out at Brookhaven National Laboratory. R.H. was supported by Contract No. DE-AC02-76CH00016 with the U.S. Department of Energy and its Division of Chemical Sciences, Office of Basic Energy Sciences. M.N., K.N., and N.K. were supported by the Monbusho International Scientific Research Program.

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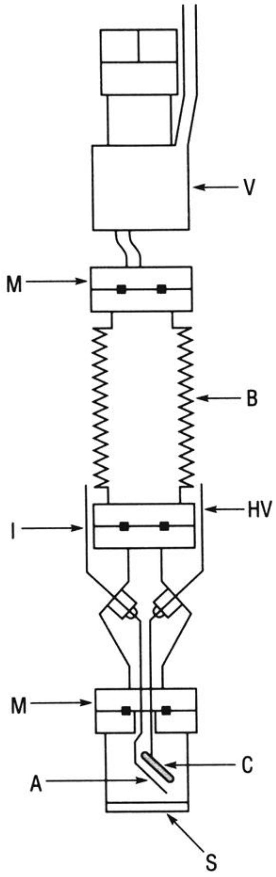

FIG. 1. Schematic of sample cell. *V*, valve; *M*, custom miniconflat flange; *B*, stainless-steel bellows; *I*, current lead; HV, high-voltage lead; *C*, Zn photocathode; *A*, 90%-transparent Ni mesh grid; *S*, sapphire window.