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Diffusion of pseudospherical molecules: An investigation on the effects of dipole moment

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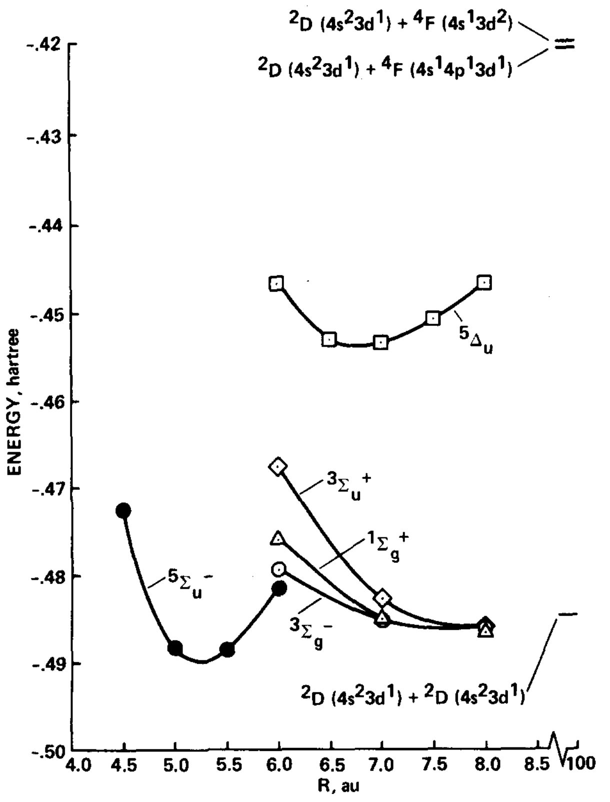

FIG. 1. Potential energy curves for the low-lying states of Sc_2 from CASSCF CI(SD) calculations. The locations of the $^2D+{}^2D$, $^2D+{}^4F(4s^1\,4p^1\,3d^1)$, and $^2D+{}^4F(4s^1\,3d^2)$ asymptotes are indicated.

two-electron σ bond. Promoting an electron of the $^3\Sigma_g^-$ state from the $4s\sigma_u$ antibonding orbital to the $3d\sigma_g$ orbital leads to the $^5\Sigma_u^-$ state which has an additional one-electron $3d\sigma$ bond and reduced 4s repulsion due to removal of an electron from the $4s\sigma_u$ orbital. Given these factors, it is not surprising that the $^5\Sigma_u^-$ state has a smaller R_e and is more stable than the $^3\Sigma_g^-$ state.

A Dunham analysis of a parabolic fit to the $^5\Sigma_u^-$ potential leads to $R_e = 5.27a_0$ and $\omega_e = 184\ \mathrm{cm}^{-1}$. The binding energy is estimated to be 0.44 eV (10.1 kcal/mol) including (i) a small differential Davidson's correction (−0.03 eV), (ii) a correction for the error in the asymptotic separation (+0.26 eV), and (iii) a correction for the energy improvement with the extended basis (+0.09 eV). The calculated R_e and ω_e values are very close to the assumed values. In the limit of *no* 3*d* interactions $^4F + {}^2D$ leads to a molecular degeneracy of 280 which would lead to an ~16 kcal/mol decrease[2] in the experimental estimate of D_e and excellent agreement with experiment. However, the actual degeneracy will be much lower than this, possibly approaching 5, and thus the calculated D_e is smaller than current experimental estimates by at least 10 kcal/mol. The calculated ω_e is slightly smaller than the current estimate[9] of 238.9 cm^{-1} which is consistent with the underestimation of D_e.

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[6] For example, valence CI calculations with the molecular basis set lead to $^4F(4s^1\,4p^1\,3d^1)$ 0.50 eV too low with respect to $^4F(4s^1\,3d^2)$.

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NOTES

Diffusion of pseudospherical molecules: An investigation on the effects of dipole moment

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Diffusion of pseudospherical solute molecules with Td symmetry has been studied recently.[1–4] The diffusivities for these solutes in solvents of compact molecules have been successfully treated with a rough-hard-sphere (RHS) model.[3,4] In that model, the transport coefficients are dependent on particle mass, temperature, fluid density, particle size, and a constant accounting for the translation-rotation coupling.[5,6] The data for solvents of noncompact molecules there can be equally well described by the same model provided that a solvent dependent translation-rotation coupling constant is used. Other diffusion data of symmetrical molecules have also been successfully analyzed[6–15] in terms of the RHS theory. Thus, all results can be considered as in general agreement with the basic assumption made in that theory. In the rough-hard-sphere theory, it is assumed[5] that the molecular motion in a liquid is determined primarily by the harsh repulsive parts of the intermolecular forces. Attractions and other forces which vary slowly in space play only a minor role. Unfortunately, analyses of diffusion data for molecules possessing dipole moments are few, and the range of applicability of the RHS theory has not been critically tested. It appears that still little is known about the effects of dipole moment on diffusion. For this reason, we have continued diffusion measurements of pseudospherical solutes to include molecules capable of forming stronger intermolecular interactions.

In this note we report the mutual diffusion coefficients of CCl_4, CH_3CCl_3. $(CH_3)_2CCl_2$, and $(CH_3)_3CCl$ at infinite dilution in acetone, methanol, ethanol, and n-decane at 298.15 ± 0.02 K. The solvents in this study are representatives of protic, aprotic, and hydrocarbon solvents. The solute molecules are all different in dipole moment, but more importantly they are of the same size and shape.

Mutual diffusion coefficients at trace concentration were measured by using the chromatographic peak-broadening technique.[16–18] The apparatus was similar in design to that reported elsewhere.[1,2] In this study, however, an HPLC system (Waters Associates) which contains a solvent delivery module with septum injector (Model 6000A) and a differential refractometer (Model R401) was utilized. The diffusion tube was a 85.7 m length of 304 stainless steel tube of 1.59 mm o.d. and 0.98 mm i.d. (Superior Tube Co.). It was coiled in a circle with a diameter of about 40 cm and immersed in a water bath controlled to within ± 0.02 K. Temperatures were measured by using a Beckmann thermometer calibrated with a certified thermometer (Baird and Tatlock, No. GDZ27736). The temperature of the refractometer cell was controlled by circulating water from the thermostat bath. The solvent flow rate was adjusted so that the constant volume flow was between 0.1 to 0.2 ml per minute. The pumping rate was equivalent to 0.22 to 0.44 cm s^{-1} in the diffusion tube. At the end of the diffusion tube, the solute dispersion peak was detected by the differential refractometer and recorded with a chart recorder (Servoscribe 2s, type RE571). The diffusion coefficients were determined from the expression[19]

$$D_{12}=0.2310R^2t_r/(W_{1/2})^2\ ,$$

where D_{12} is the mutual diffusion coefficient, R is the internal radius of the diffusion tube, t_r is the residue time of the solute in the tube, and $W_{1/2}$ is the width at half-height of the eluted peak.

In this experiment, the solvents acetone (99.5%+, BDH), ethanol (99.5%+, Ajax), methanol (99.5%, BDH), and n-decane (99%+, TCI) were used as received. The solutes 2, 2-dichloropropane (96%, TCI) and 2-chloro-2-methylpropane (99%, Seelze-Hanover) were purified by fractional distillation; solutes carbon tetrachloride (99.5%, Carlo Erba) and 1, 1, 1-trichloroethane (99.5%+, BDH) were used without further purification.

The diffusion coefficients as determined by the chromatographic broadening apparatus are summarized in Table I. These values are the averages resulting from three or more diffusion measurements. The uncertainty listed is the average absolute error. Also shown in parenthesis in Table I are previous values[1,2,20] for carbon tetrachloride and neopentane. Wherever comparisons are available, the previous data and the present data are in excellent agreement, the average deviation being ±1.1%. Table I also includes the values of the dipole moment and molecular diameter of the solute molecules. It should be noted that a 1% change in solute core diameter only produces typically a 2% variation in the mutual diffusion coefficient.[4,14]

The following points emerge from the data presented in Table I:

(1) The mutual diffusion coefficients are approximately equal in each solvent. (Exception may be 2, 2-dichloropropane in n-decane which shows a small ≃ 13% deviation from the average.) The coefficients are therefore generally insensitive to the molecular mass and dipole moment of the solute molecules.

(2) That dipole moment does not affect the experimental diffusion coefficients in this work further justifies the basic assumption in the RHS theory, i.e., attractive interactions and other forces which are supposedly slowly varying in space are unimportant in determining the molecular dynamics of liquids. This implies not only that the range of validity of that assumption is wider than previously known, but also that we have a better fundamental picture of the molecular motion in dense fluids.

(3) Since the CCl_4 data can be interpreted[3] in terms of the rough-hard-sphere theory, it follows from the insensitivity of mass and dipole moment on diffusion that other data in this study can also be described by that theory.

(4) Experimental determination of diffusion coefficients for polar solutes with equal size and shape pro-

TABLE I. Limiting mutual diffusion coefficient ($D_{12}\times10^9$ m^2 s^{-1}) at 298.2 K.

	Molecular diameter[a] (σ, nm)	Dipole moment[b] (D)	Solvent			
			Acetone	Methanol	Ethanol	n-Decane
CCl_4	0.5537	0	3.61 ± 0.03 (3.63 ± 0.03)[c]	2.27 ± 0.03 (2.25 ± 0.02)[c]	1.47 ± 0.01 (1.50)[d]	1.72 ± 0.02 (1.70 ± 0.02)[c]
$MeCCl_3$	0.5549	1.78	3.65 ± 0.03	2.28 ± 0.02	1.47 ± 0.01	1.78 ± 0.02
Me_2CCl_2	0.5562	2.27	3.62 ± 0.03	2.32 ± 0.03	1.48 ± 0.02	1.45 ± 0.02
Me_3CCl	0.5574	2.13	3.62 ± 0.03	2.27 ± 0.03	1.46 ± 0.01	1.65 ± 0.02
Me_4C	0.5587	0	···	···	···	(1.71 ± 0.01)[c]

[a] The values are calculated from the average van der Waals volumes of Refs. 21–24.

[b] *CRC Handbook of Chemistry and Physics*, 62nd ed., edited by R. C. Weast (Chemical Rubber, Boca Raton, Florida, 1981).

[c] From Refs. 1 and 2.

[d] From Ref. 20.

vides a simple and straightforward method for testing the effects of dipole moment on diffusion.

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Multiphoton ionization spectroscopy of Al_2Me_6: Detection of the *np* ^2P_J and *nf* ^2F_J Rydberg states of aluminium[a)]

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Transition metal atoms may be generated in the gas phase via the multiple photon dissociation of organometallic compounds by high power pulsed UV/visible lasers.[1] Sequential multiphoton ionization MPI of the nascent atom occurs at wavelengths corresponding to one-photon or two-photon resonant transitions.[2] To date, the technique has been applied to first row transition elements[1(a)–1(h)] and heavier transition elements Mo[1(a)] and W.[1(b)]

Interpretation of the MPI spectra of group III elements is simplified even at wavelengths approaching the two-photon ionization limit. For example, the first excited state of Al(I), $4s\ ^2S_{1/2}$ lies 25 347.8 cm^{-1} above the Al($3p\ ^2P^0_{1/2}$) ground state[3,4]; more than half-way to the ionization limit.[3] One-photon resonances occur at wavelengths shorter than 414.26 nm so that 1R3I lines do not occur at longer wavelengths. Single photon optical spectroscopy of the $np\ ^2P_J$ and $nf\ ^2F_J$ Rydberg states of Al(I) has not been reported above $n = 7$ and 10, respectively.[4] Two-photon resonant MPI is effective in identifying higher ^2P_J and ^2F_J Rydberg states with an ultimate resolution decided by collisional,[5] field,[6] and power broadening[7] of the resonance lines.

We report the first example of MPI spectroscopy of the main group metal Al, generated from the MPD of trimethylaluminium Al_2Me_6. Rydberg states in the $np\ ^2P_J$ and $nf\ ^2F_J$ series have been identified for $n < 18$ and 17, respectively, employing techniques previously described.[1] Ion signals were contingent upon the presence of Al_2Me_6 (electronic grade, Alfa Inorganics; 0.1–1 Torr) in the ionization cell.

The two-photon resonant MPI spectrum of the $3p\ ^2P_{1/2,3/2}-np\ ^2P_{1/2,3/2}$ and $3p\ ^2P_{1/2,3/2}-nf\ ^2F_{5/2,3/2}$ transitions in Al(I) was recorded in the region 410–650 nm. The spectral dependence of the ionization signal showed the 2R3I atomic Al(I) lines superimposed on a weak continuous background current. A portion of the complete spectrum is shown in Fig. 1 corresponding to the $3p\ ^2P_J-6p\ ^2P_J$ and $3p\ ^2P_J-5f\ ^2F_J$ Rydberg transitions. No other lines were detected in the spectral region investigated.[8] The entire spectrum formed two simple Rydberg series attaining a common limit in excellent agreement with the literature value[4] of 48 278.37 cm^{-1}. Spin-orbit multiplet splitting was observed for the lower members of the $np\ ^2P_J$ series, $n = 5$ and 6 in agreement with the single photon intervals.[4] Spin-orbit splitting in the higher ^2P_J levels or the ^2F_J series was not resolved. The corresponding Rydberg plots for both series are shown in Fig. 2 for $n < 18$ where, for terms common to single photon and 2R3I investigations, the wavelengths are in agreement to within ±0.01 nm. The measured values of the Rydberg constant for the ^2P_J and ^2F_J series are 106 406 ± 684 and 108 095 ± 617 cm^{-1} and the quantum defects are 1.382 and 6.436×10^{-2}, respectively. Transitions with increasing L are more intense than the

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