Intermolecular Forces of the Heavy Rare Gases

J. C. Rossi, and F. Danon

Citation: The Journal of Chemical Physics **43**, 762 (1965); doi: 10.1063/1.1696808
View online: https://doi.org/10.1063/1.1696808
View Table of Contents: http://aip.scitation.org/toc/jcp/43/2
Published by the American Institute of Physics

PHYSICS TODAY
WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY
MASTERBOND
ADHESIVES | SEALANTS | COATINGS

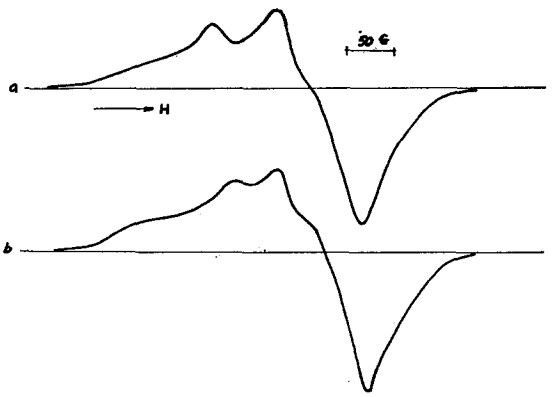

FIG. 2. (a) ESR spectrum of [Ag II, $Cd(py)_4$] S_2O_8 with Ag:Cd=1:10. (b) Theoretical reconstruction of the above spectrum.

(2) Samples of pure [Ag II$(py)_4$]S_2O_8 give spectra which can be interpreted as belonging to a rhombic g tensor with principal values reported by Ref. (2), [Fig. 1(b)]. We call this the c spectrum. The same spectrum is obtained for more dilute samples, whenever the concentration of Ag II exceeds about 20%.

(3) At concentrations below 20% Ag, a gradual change occurs from one type of spectrum to the other. At any concentration the spectrum can be reconstructed theoretically by superposition of the spectra of Types c and d in varying proportions [Fig. 2(a) and 2(b)].

The nature of the c spectrum is not well understood. Assuming that it arises from exchange-coupled pairs of Ag^{++} ions in their triplet state, we reconstructed theoretically the spectra in the concentration range: Ag:Cd=0.02 to 0.2, by superposition of the c and d spectra. The relative intensity of the c spectrum was taken to be proportional to the probability of finding pairs of neighboring silver complexes in the lattice. The number of neighbors of each silver ion was found from the best fit of the experimental data. Consistency was obtained for $n=4$.

This interpretation is in contradiction with some magnetic susceptibility measurements[1] indicating Curie's law dependence down to 1.6°K. Previous measurements,[3] however, showed antiferromagnetic behavior with a Weiss constant $\theta=-26$°K in the case of the pure, undiluted Ag II complex.

The principal g values of the c spectrum are consistent with this latter interpretation, although they could be derived theoretically only if the relative orientations of the sites in the unit cell of the crystal were known.

The hyperfine structure of the d spectrum: In the region of the spectrum corresponding to the axial direction in the complex, we observe 11 lines; in the region corresponding to directions perpendicular to the symmetry axis, there are 10 lines with some indication of not well resolved additional structure. The spectrum is interpreted assuming that there is hyperfine interaction with the silver nucleus ($I^{Ag}=\frac{1}{2}$) and also with four nitrogen nuclei, each with $I^N=1$, from the pyridine ligands in a square-planar arrangement. If the nitrogens are equivalent, we obtain a total of $(2I^{Ag}+1)(8I^N+1)=18$ lines, which may partially overlap. We find $A_{||}(Ag)=34$; $A_{\perp}(Ag)=22$; $A_{||}(N)=17$; $A_{\perp}(N)=22$, all in units of 10^{-4} cm^{-1}. The fact that $A_{\perp}(Ag)=A_{\perp}(N)$ and $A_{||}(Ag)=2A_{||}(N)$ accounts for the number of lines and intensity distribution observed.

We have recently been able to grow mixed single crystals of [Ag II, $Cd(py)_4$]S_2O_8, large enough to allow single-crystal measurements to be made. Work on their ESR spectra is now in progress. We hope to identify the origin of the c spectrum, to find more accurate values for the spin Hamiltonian of the d spectrum and to study the additional structure of this spectrum, perhaps due to the two Ag isotopes.

[1] H. M. Gijsman, H. J. Gerritsen, and J. van der Handel, Physica **20**, 15 (1954).
[2] J. A. McMillan and B. Smaller, J. Chem. Phys. **35**, 1698 (1961).
[3] N. Perakis and L. Capatos, J. Phys. Radium **9**, 27 (1938).

Intermolecular Forces of the Heavy Rare Gases

J. C. ROSSI AND F. DANON
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina

(Received 11 March 1965)

TWO alternative solutions to the problem of the stability of the crystal structures of the heavy rare gases have recently been presented.[1,2] Jansen uses third-order perturbation theory to calculate the contribution of exchange forces to the cohesive energies of the crystals. We have shown that the theory of dispersion force as formulated by Kihara[3] gives a three-body interaction energy contribution to the total energy of the crystals high enough to correctly predict their relative stability. The calculation was done assuming a Lennard-Jones pair potential function and using the experimental values[4] of the lattice constant to evaluate three-body and zero-point energy effects.

TABLE I. Parameters of the pair potential.

	Lennard-Jones model		Molecular core model		
	U_0/k (°K)	r_0 (Å)	U_0/k (°K)	ρ_0 (Å)	d (Å)
Argon	117.5	3.940	140.6	3.440	0.275
Krypton	164.1	4.294	194.8	3.748	0.300
Xenon	222.7	4.595	261.7	4.095	0.328

TABLE II. Cohesive energy and relative stability of heavy rare gases.

	Lennard-Jones model			Molecular core model			Experimental values	
	Sublimation energy E_c (cal/mole)	Stability E_c-E_h (10^2 cal/mole)	Nearest-neighbor distance (Å)	Sublimation energy E_c (cal/mole)	Stability E_c-E_h (10^2 cal/mole)	Nearest-neighbor distance (Å)	Sublimation energy (cal/mole)	Nearest-neighbor distance (Å)
Ar	1626	4.7	3.934	1729	0.8	3.752	1846[a] 1806[b]	3.756[d,e]
Kr	2343	4.3	4.269	2458	−2.7	4.072	2666[a] 2601[b]	3.991[d]
Xe	2989	−10.3	4.604	3148	−18.0	4.471	3828[c]	4.335[d,f]

[a] R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. (London) **78**, 1462 (1961).
[b] L. S. Salter, Trans. Faraday Soc. **59**, 657 (1963).
[c] E. Whalley and W. G. Scheneider, J. Chem. Phys. **23**, 1644 (1955).
[d] L. H. Bolz and F. A. Mauer, See Ref. 8(c).
[e] C. S. Barret and L. Meyer, J. Chem. Phys. **41**, 1078 (1964).
[f] D. R. Sears and H. P. Klug, J. Chem. Phys. **37**, 3002 (1962).

The purpose of the present note is to point out (i) when the calculation is done by minimizing the total energy of the crystal as given by Eq. (1) the values obtaiend for the lattice constant and the cohesive energy disagree seriously with experiment if one uses Lennard-Jones 6–12 pair potential and (ii) if the pair potential of Kihara's core model of molecules[5] is used, significantly better results are obtained.

The pair potential must be deduced from properties which depend only on binary interactions.[6] In both cases it was constructed from a low-density property, i.e., the second virial coefficient. The parameters were obtained by automatic computation, minimizing the rms deviation between experimental and calculated values of $B(T)$. This is the best "gas-phase intermolecular potential" and it constitutes a severe test to use it in studying solid-state properties. When calculations are done taking proper account of the zero-point energy and the three-body effects only the Kihara potential gives a satisfactory result.

The cohesive energy of the crystal is given by the minimum of

$$\Phi(a)=\tfrac{1}{2}\sum_{i=1}^{i=\infty}n_iU(\rho_i)+\frac{9}{8}\left(\frac{5}{3}\right)^{\frac{1}{3}}\left(\frac{h^2}{6\pi^2m}\right)^{\frac{1}{3}}\times\left[\sum_{i=1}^{\infty}n_i\left(\frac{1}{\rho_i+d}\right)\frac{\partial U(\rho_i)}{\partial\rho_i}+\frac{1}{2}\frac{\partial^2U(\rho_i)}{\partial\rho_i{}^2}\right]^{\frac{1}{3}}+\frac{K\nu}{a^9} \quad (1)$$

with respect to a, the nearest-neighbor distance, and where m is the mass of the molecule, n_i is the number of molecules at the distance ρ_i from a central molecule, K is the geometry dependent part of the three-body energy summed over the structure,[7] and ν the corresponding coefficient as given by Kihara.[3] $U(\rho_i)=U_0[(\rho_0/\rho_i)^{12}-2(\rho_0/\rho_i)^6]$ is the Kihara's pair potential[5a] and $\rho_i=\gamma(i)a-d$; $\gamma(i)$ depends on the geometry of the lattice and d is the core diameter.

The failure of the Lennard-Jones pair potential in describing solid-state properties accurately should not be surprising in view of extensive studies made of the inadequacy of this potential.[5a,8] It has been shown by one of us[9] and later by other investigators[10] that the Kihara potential function is considerably better than the Lennard-Jones for the gas-phase equilibrium properties and fits the transport properties as well.[11]

The parameters of the pair potential used are indicated in Table I. Results of the present calculation[12] are given in Table II. The stability of the crystal structure is now correctly predicted for Kr and Xe. The difference in energy between the two structures of solid argon is now smaller than in previous calculations ignoring many body effects[13] but still favors the hexagonal close packing. This may be attributed to the assumption of harmonic vibrations used in the evaluation of zero-point energy in Eq. (1). It has recently been shown[14] that the anharmonic contribution to the free energy of crystals at 0°K is very significant for neon and argon and favors the fcc structure over the hcp. This theory, however, does not permit a refined quantitative calculation at the present time.

The present treatment neglects interactions of higher order than the third. Bade[15] has shown that fourth-order energy is negative and makes a significant contribution to the cohesive energy. This would probably explain the difference between calculated and observed values of the cohesive energies and would also decrease the calculated lattice parameter.

It should be noticed that Lennard-Jones' potential correctly predicts the structure of solid xenon. Solid neon is not considered in the present study because quantum effects in Ne are important even in the gas-phase properties at low temperature. It is important to point out that the core size d is not an extra adjustable parameter in the present calculation as it is in other works.[10,11] By using a simple relationship derived previously,[5b] d is related to ρ_0 so that the Kihara potential is still a two-independent-parameter potential function. We are now studying gas-phase properties of rare gases using the Kihara potential

and complete results of these calculations will soon be published.

[1] L. Jansen, Phys. Rev. **135**, A1292 (1964).
[2] J. C. Rossi and F. Danon, J. Phys. Chem. Solids (to be published).
[3] T. Kihara, Advan. Chem. Phys. **1**, 267 (1958).
[4] E. R. Dobbs and C. C. Jones, Rept. Progr. Phys. **20**, 516 (1957).
[5] (a) T. Kihara, Rev. Mod. Phys. **25**, 831 (1953); (b) F. Danon and K. S. Pitzer, J. Chem. Phys. **36**, 425 (1962).
[6] B. J. Alder, Ann. Rev. Phys. Chem. **12**, 195 (1961); R. J. Munn, J. Chem. Phys. **40**, 1439 (1964).
[7] B. M. Axilrod, J. Chem. Phys. **19**, 719, 724 (1951).
[8] W. B. Brown and J. S. Rowlinson, Mol. Phys. **3**, 35 (1960); G. Boato and G. Casanova, Physica **27**, 517 (1961); G. C. Pollack, Rev. Mod. Phys. **36**, 748 (1964).
[9] F. Danon, Ph.D. thesis, University of California, Berkeley, 1962, UCRL 10029.
[10] P. G. Francis and C. R. Luckhurst, Trans. Faraday Soc. **59**, 667 (1963); A. E. Sherwood and J. M. Prausnitz, J. Chem. Phys. **41**, 413 (1964).
[11] J. A. Barker, W. Fock, and F. Smith, Phys. Fluids **7**, 897 (1964).
[12] Calculations were performed with the aid of the Mercury computer at the Instituto de Cálculo of this University.
[13] T. Kihara and S. Koba, J. Phys. Soc. Japan **7**, 348 (1952); L. Jansen and L. M. Dawson, J. Chem. Phys. **23**, 482 (1955).
[14] D. C. Wallace, Phys. Rev. **131**, 2046 (1963); **133**, A153 (1964).
[15] W. L. Bade, J. Chem. Phys. **27**, 1280 (1957); **28**, 282 (1958).

Relaxation Mechanisms in Ethane at the Ice Point*

B. H. Muller and J. F. Harmon
University of Wyoming, Laramie, Wyoming
(Received 5 March 1965)

In order to separate the various contributions to spin–lattice relaxation in liquid ethane, we have measured T_1, the proton spin–lattice relaxation time in mixtures of CH_3CH_3 with CD_3CD_3, and in pure CH_3CD_3, CHD_2CHD_2, and CHD_2CD_3 at the ice point. T_1 was measured by observing the recovery of the spin echo to its equilibrium value after a saturating pulse at 30 Mc/sec. Oxygen present in the samples was removed by a gettering technique.[1] The mixture samples were prepared by progressively diluting CD_3CD_3 with CH_3CH_3. The concentration was measured by observing pressures before and after addition of CH_3CH_3 in the same volume.

Our results for the mixture experiment are presented in Fig. 1 in which the relaxation rate, $R=1/T_1$, is plotted as a function of the concentration of CD_3CD_3. As expected, the data are fitted by a straight line whose intercepts at 0% and 100% CD_3CD_3 concentration allow us to get values for both the intermolecular R_B and the total intramolecular contributions to relaxation in pure ethane. The intercept of the least-squares line at 0% CD_3CD_3 is in excellent agreement with Noble's measurement of T_1 in CH_3CH_3 at the ice point.[2]

Our measurements of the proton T_1 in the deuterated modifications of ethane, together with plausible assumptions about the dependence of the various terms on deuteration, now allow us to separate the total intramolecular contribution into the part due to dipolar interactions, R_A, and the part due to spin–rotational interactions, R_C.

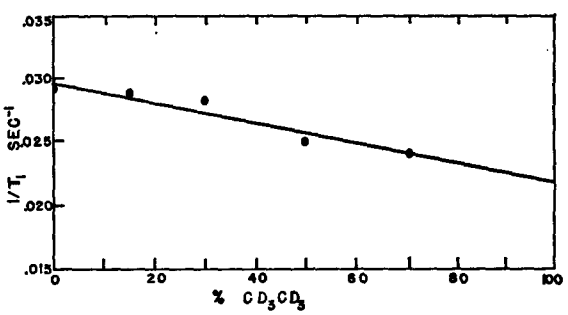

FIG. 1. The spin–lattice relaxation rate $1/T_1$ of protons in CH_3CH_3 as a function of the dilution of CH_3CH_3 with CD_3CD_3.

Both R_A and R_B are functions of the number and location of the protons and deuterons as described by the following equation:

$$\begin{aligned}(1/T_1)_{n',n''} &= R_A(n', n'') + R_B(n', n'') + R_C \\ &= [R_A(0,0)/(2+3\alpha)]\{[(2-n')+n'\beta] \\ &\quad +\alpha[(3-n'')+n''\beta]\} \\ &\quad +\tfrac{1}{6}R_B(0,0)\{[6-(n'+n'')] \\ &\quad +\beta[n'+n'']\} + R_C,\end{aligned}$$

where n' is the number of deuterons on the same methyl group as the proton whose relaxation time is being calculated and n'' is the number of deuterons on the other methyl group; $R_A(0, 0)$, $R_B(0, 0)$, R_C are, respectively, the contributions to $1/T_1$ for CH_3CH_3 due to the interactions usually assumed to be responsible for relaxation for spin $\frac{1}{2}$ nuclei in polyatomic mole-

TABLE I. Contributions to spin-lattice relaxation in ethane.

Sample	n'	n''	Temperature (°K)	T_1 (sec)	$1/T_1$ (10^{-2} sec^{-1})	$R_B(n', n'')$ (10^{-2} sec^{-1})	R_C (10^{-2} sec^{-1})	$R_A(n', n'')$ (10^{-2} sec^{-1})
CH_3CH_3	0	0	273.3	33.8±0.6	2.96	0.82	1.24	0.83
CH_3CD_3	0	3	273.7	43±2	2.33	0.43	1.24	0.72
CHD_2CHD_2	2	2	273.4	56±6	1.79	0.30	1.24	0.07
CHD_2CD_3	2	3	273.8	83±16	1.20	0.17	1.24	0.04