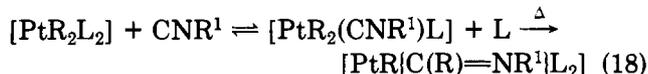


coordinate intermediate by the chelating ligand or to a more difficult phosphine displacement, again because of the chelate effect.

In the case of diorganoplatinum complexes, reaction with CO causes displacement of one tertiary phosphine from  $[\text{PtR}_2\text{L}_2]$  ( $\text{L} = \text{PPh}_3$  or  $\text{PMePh}_2$ )<sup>54</sup> but no insertion, whereas no reaction occurs at all where  $\text{L}_2 =$  bidentate phosphine. With isocyanides,  $[\text{PtR}_2\text{L}_2]$  complexes undergo insertion on prolonged heating, but again the initial reaction is phosphine displacement (eq 18).<sup>57</sup> Insertion is favored by the more basic phos-



phines,  $\text{PEt}_3$  and  $\text{PMe}_2\text{Ph}$ , whereas phosphine displacement is more extensive for  $\text{L} = \text{PPh}_3$  and  $\text{PMePh}_2$ .

Complexes of less strongly bonding chelating ligands in certain cases do undergo carbonylation, however. Thus,  $[\text{PtXR}(\text{cod})]$  complexes react with CO to yield  $[\text{PtX}(\text{COR})(\text{cod})]$ ,<sup>58</sup> whereas only displacement of 1,5-cyclooctadiene by CO occurs for  $[\text{PtR}_2(\text{cod})]$ . Addition of tertiary phosphine to solutions of the resulting  $[\text{PtR}_2(\text{CO})_2]$ , however, did not induce insertion but, rather, resulted in displacement of carbon monoxide. The trigonal-bipyramidal complexes  $[\text{NiR}(\text{np}_3)]\text{BPh}_4$  ( $\text{np}_3 = (\text{Ph}_2\text{PCH}_2\text{CH}_2)_3\text{N}$ )<sup>59</sup> undergo insertion of CO, where it is supposed that reversible cleavage of the relatively weak Ni-N bond occurs on CO coordination. In the above cases the relative ease of cleavage of the metal-olefin and metal-nitrogen bonds is doubtless a major contributor to their reactivity.

(57) Treichel, P. M.; Wagner, K. P. *J. Organomet. Chem.* 1973, 61, 415.

(58) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* 1981, 20, 1636.

(59) Stoppioni, P.; Dapporto, P.; Sacconi, L. *Inorg. Chem.* 1978, 17, 718.

## Conclusions

It is apparent that a great deal is now understood about the mechanisms of carbonyl insertion at square-planar complexes. Spontaneous insertion of carbon monoxide occurs, provided certain conditions are met: these include a cis arrangement of CO and the organic group and a ligand trans to R of sufficiently high trans influence to weaken the M-R bond. These are consistent with R migration being the reaction mechanism. In addition, the insertion step is favored by a partial negative charge on R and a partial positive charge on CO. The migration will rapidly reverse unless an incoming ligand is available to stabilize the initially formed three-coordinate species. This may be a bridging halide or an added species such as tertiary phosphine.

Carbonylation of  $[\text{MXRL}_2]$  complexes proceeds by two routes, one of which involves L dissociation from the initially formed five-coordinate intermediate,  $[\text{MXR}(\text{CO})\text{L}_2]$ . The reactions are faster for palladium than for platinum and occur most readily for triarylphosphine complexes, both observations being expected in the context of a mechanism involving displacement of tertiary phosphine. Thus, the dissociative pathway (usually the major route when  $\text{L} =$  triarylphosphine) involves isomerization of, and spontaneous CO insertion from, a square-planar complex,  $[\text{MXR}(\text{CO})\text{L}]$ . The necessity for L dissociation is underlined by the inability of organoplatinum complexes containing bidentate phosphine ligands to undergo carbonylation. The five-coordinate route dominates the process in a few cases, including that involving the catalytically important  $\text{SnCl}_3$  group as "nonparticipating" anion. These, too, probably proceed by R migration, but here from a species with R at the apex of a square-pyramidal configuration.

## Pressure Effects on the Dynamic Structure of Liquids

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In recent years there has been significant progress toward a better understanding of the liquid state on the basis of theoretical and experimental work. Particularly, studies in which pressure was used as an experimental variable have contributed in a major way to our knowledge of liquids. In view of my own expertise the following discussion is limited to NMR and laser Raman scattering studies of liquids at high pressure.<sup>1-5</sup>

It is well-known that NMR relaxation experiments provide detailed information about molecular motions and interactions in liquids, including reorientational

correlation times, angular momentum correlation times, and diffusion coefficients. Laser Raman scattering experiments are restricted usually to simpler liquids but provide, on the other hand, more detailed information about a specific dynamic process in a liquid. From the analysis of Raman bands using well-developed procedures, we can actually obtain the detailed time dependence of a correlation function.

The main goal of this Account is to show that pressure is an essential experimental variable in all studies that attempt to improve our basic understanding of the liquid state. The use of high pressure to investigate the

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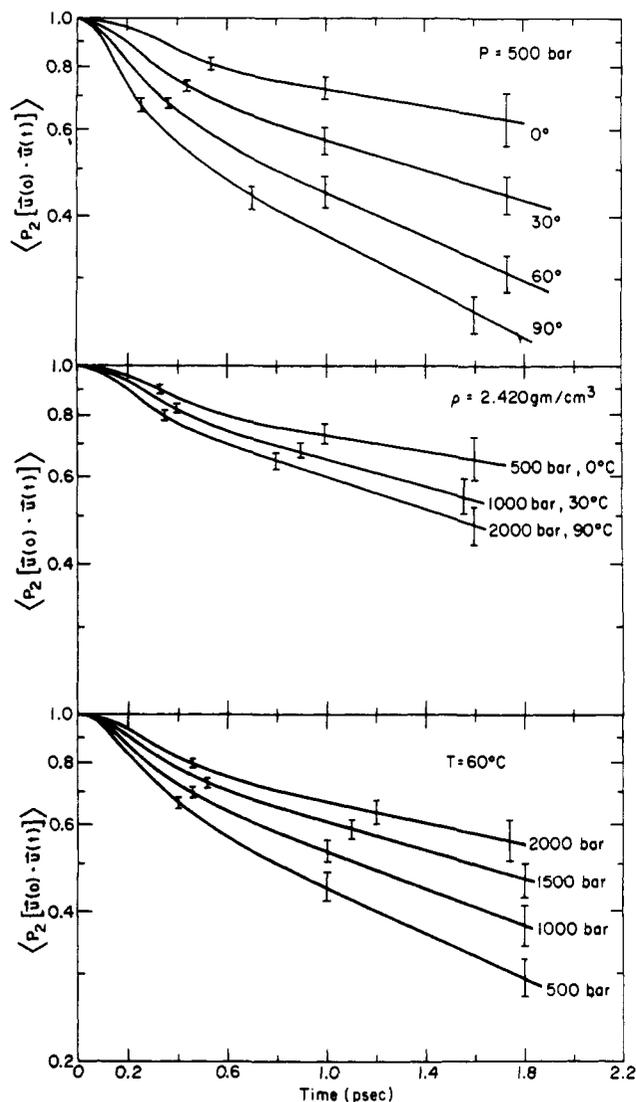
(1) Hasha, D. L.; Eguchi, T.; Jonas, J. *J. Am. Chem. Soc.* 1982, 104, 2290.

(2) Schindler, W.; Jonas, J. *J. Chem. Phys.* 1980, 72, 5019.

(3) Schroeder, J.; Jonas, J. *Chem. Phys.* 1978, 34, 11.

(4) Zerda, T. W.; Perry, S.; Jonas, J. *Chem. Phys. Lett.* 1981, 83, 600.

(5) Hegemann, B.; Jonas, J. *J. Chem. Phys.* 1983, 79, 4683.

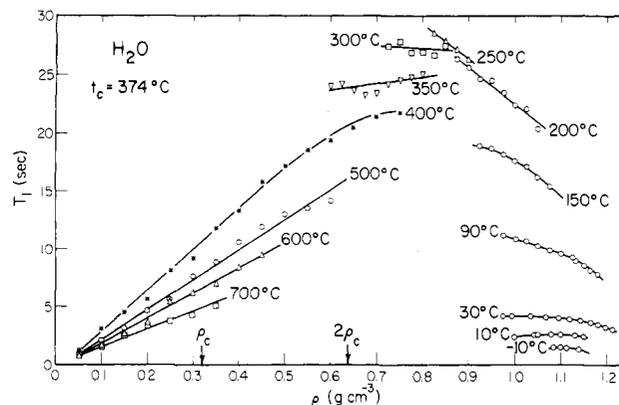


**Figure 1.** Reorientational correlation functions for  $\text{CH}_3\text{I}$  under isobaric (top), isochoric (center), and isothermal (bottom) conditions.

density effects on various dynamic processes provides the common theme in this account, which covers several different topics that illustrate the range of problems that can be studied.

There are several fundamental reasons for performing experiments on liquids at high pressures. If one investigates the temperature dependence of some dynamic process in a liquid at atmosphere pressure, the experimental data reflect both the change of the kinetic energy of the molecules and the change in the average volume available for the motion of the molecule. Only by carrying out a high-pressure experiment can one separate the effect of temperature and density on the molecular motions and interactions in a liquid. In order to provide a rigorous test of a theoretical model of a liquid or of a model of a specific dynamic process, one has to perform isobaric, isochoric, and isothermal experiments. An example of the relative effect of density and temperature on molecular motions is given in Figure 1, which shows the reorientational correlation function obtained from the Raman line shapes in liquid methyl iodide,<sup>6</sup> a symmetric top molecule. The corre-

(6) Campbell, J. H.; Fisher, J. F.; Jonas, J. J. *Chem. Phys.* 1974, 61, 346.



**Figure 2.** Proton NMR spin-lattice relaxation time,  $T_1$ , in water as a function of density, over the temperature range from  $-10$  to  $700$  °C.

lation function describes the reorientation of  $\text{CH}_3\text{I}$  about axes perpendicular to the main symmetry axis. The large difference between the isobaric and the isochoric experiment is readily apparent from this figure.

In addition, the use of pressure enables one to investigate liquids well above their normal boiling point and also allows the study of supercritical dense fluids. The temperature and density range covered in such high-pressure experiments is very broad, as it is illustrated in Figure 2. This figure shows the portion NMR spin-lattice relaxation times,  $T_1$ , in water<sup>7</sup> measured both in the low temperature ( $T < 30$  °C) anomalous region and in the high-temperature ( $T < 30$  °C) anomalous region and in the high-temperature ( $T > 400$  °C) supercritical region. The temperature and density dependence of the proton  $T_1$  is typical for the case where two relaxation mechanisms with opposite temperature and density dependence contribute to the observed  $T_1$ . At lower temperatures dipolar interactions dominate, whereas spin-rotation interactions provide the main source of relaxation in the supercritical regions.

Yet another reason for the use of high pressure is related to a rather specialized application. For example, taking advantage of the specific form of the phase diagram of water or heavy water, one can investigate liquid water<sup>8</sup> at temperatures below  $0$  °C; at high pressures water is still a liquid, even at  $-15$  °C. The anomalous motional behavior of water with initial compression is most pronounced below  $0$  °C.

### Transport and Relaxation in Liquids

Before discussing the application of high-resolution NMR spectroscopy at high pressure, it seems appropriate to indicate the nature and extent of our earlier systematic studies of transport and relaxation properties of various liquids. We investigated the applicability and validity of hard sphere models<sup>9-11</sup> for diffusion, viscosity, and angular momentum transfer in dense liquids and in supercritical fluids. The liquids we studied ranged from  $\text{CF}_4$  to hydrogen-bonded liquids such as  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , and  $\text{CH}_3\text{OH}$ . They are listed in Table I together with the properties investigated and the appropriate references. The most important NMR

(7) Lamb, W. J.; Jonas, J. J. *Chem. Phys.* 1981, 74, 913.

(8) DeFries, T.; Jonas, J. J. *Chem. Phys.* 1977, 66, 896.

(9) Alder, B. J.; Gass, D. M.; Wainwright, T. E. *J. Chem. Phys.* 1970, 53, 3813.

(10) Chandler, D. *J. Chem. Phys.* 1974, 60, 3500, 3508.

(11) Chandler, D. *J. Chem. Phys.* 1975, 62, 1358.

Table I  
Summary of Transport and Relaxation Properties of Liquids Studied at High Pressure

liquid	information <sup>a</sup>	liquid	information <sup>a</sup>
CH <sub>3</sub> I	R, V, $\rho$ , $\eta$ (RS) [6]	toluene-d <sub>8</sub>	R, $\eta$ , $\rho$ (N) [13]
CD <sub>3</sub> I	R (N) [6]	benzeneacetonitrile	R (N) [14]
CHCl <sub>3</sub>	R, V, $\rho$ (RS) [15]	benzotrifluoride	R (N) [16]
CDCl <sub>3</sub>	R, V, $\rho$ (RS) [15]	pyridine	D, $\eta$ , $\rho$ (N) [17]
CH <sub>3</sub> CN	V, $\rho$ (RS) [18]	CH <sub>3</sub> OH	D, $\eta$ , $\rho$ (N) [20]
CD <sub>3</sub> CN	V, $\rho$ , R (RS, N) [18, 19]	CD <sub>3</sub> OH	V (RS) [21]
propyne	R, V (RS) [22]	methylcyclohexane	D, $\eta$ , $\rho$ (N) [23]
C <sub>6</sub> H <sub>6</sub>	D, $\eta$ , $\rho$ , V (N, RS) [24]	C <sub>6</sub> D <sub>6</sub> F	R, $\eta$ (N) [25]
C <sub>6</sub> D <sub>6</sub>	V (RS) [26]	C <sub>6</sub> D <sub>5</sub> Cl	R, $\eta$ (N) [27]
CF <sub>4</sub>	J, R, $\rho$ , $\eta$ (RS, N) [28]	C <sub>6</sub> H <sub>5</sub> Br	R, $\eta$ (N) [27]
CF <sub>4</sub> in Ar, Ne	J, R (RS, N) [28b, 29]	C <sub>6</sub> H <sub>5</sub> I	R, $\eta$ (N) [27]
SF <sub>6</sub>	J, R, $\rho$ , D, $\eta$ (RS, N) [30]	H <sub>2</sub> O	R, J, D (N) [31]
C <sub>4</sub> F <sub>8</sub>	J, V, D (RS, N) [32]	D <sub>2</sub> O	D, R (N) [33]
CCl <sub>3</sub> F	J (N) [34]	Si(CH <sub>3</sub> ) <sub>4</sub>	D, $\eta$ , $\rho$ , V (N, RS) [24a, 35]
acetone	V, $\rho$ (RS) [36]	Ge(CH <sub>3</sub> ) <sub>4</sub>	V, $\rho$ (RS) [35]
ethylene carbonate	V, $\rho$ (RS) [37]	Sn(CH <sub>3</sub> ) <sub>4</sub>	V, $\rho$ (RS) [35]
isobutylene	V, $\rho$ (RS) [38]	C(CH <sub>3</sub> ) <sub>4</sub>	V, $\rho$ (RS) [35]
acetaldehyde	V, $\rho$ (RS) [37]	n-C <sub>4</sub> H <sub>10</sub>	D, $\eta$ , $\rho$ (N) [39]
glycerol-d <sub>4</sub>	R, $\eta$ , $\rho$ (N) [40]	n-C <sub>5</sub> H <sub>12</sub>	D, $\eta$ , $\rho$ (N) [39]
glycerol-d <sub>3</sub>	R, $\eta$ , $\rho$ (N) [40]	DEHP <sup>b</sup>	R (N) [41]
dioxane-D <sub>2</sub> O	R, D, $\eta$ , $\rho$ (N) [43]	isopropylbenzene	R, $\eta$ , $\rho$ (N) [42]
cyclohexane	D, $\eta$ , $\rho$ , V (N, RS) [44]	aqueous electrolytes	R (N) [45]

<sup>a</sup> Property studied: D, diffusion;  $\eta$ , viscosity; J, angular momentum correlation time; R, rotational relaxation; V, vibrational relaxation;  $\rho$ , density. Symbol in parentheses denotes technique used: N, NMR; RS, laser Raman scattering. References are given in brackets. <sup>b</sup> DEHP, bis(ethylhexyl) phthalate.

results have been discussed in a recent review article.<sup>12</sup> Table I also shows that we have carried out a number

- (12) Jonas, *J. Science* **1982**, *216*, 1176.  
 (13) Wilbur, D. J.; Jonas, *J. J. Chem. Phys.* **1975**, *62*, 2800.  
 (14) DeZwaan, J.; Jonas, *J. J. Phys. Chem.* **1973**, *77*, 1768.  
 (15) (a) Schroeder, J.; Schiemann, V. H.; Jonas, *J. Mol. Phys.* **1977**, *34*, 1501. (b) Schroeder, J.; Schiemann, V. H.; Jonas, *J. J. Chem. Phys.* **1978**, *69*, 5479.  
 (16) Bull, T. E.; Barthel, J. S.; Jonas, *J. J. Chem. Phys.* **1971**, *59*, 3663.  
 (17) Fury, M.; Munie, G.; Jonas, *J. J. Chem. Phys.* **1979**, *70*, 1260.  
 (18) Schroeder, J.; Schiemann, V. H.; Sharko, P. T.; Jonas, *J. J. Chem. Phys.* **1977**, *66*, 3215.  
 (19) Bull, T. E.; Jonas, *J. J. Chem. Phys.* **1970**, *53*, 3315.  
 (20) Akai, J. A.; Jonas, *J. J. Chem. Phys.* **1977**, *66*, 4946.  
 (21) Schiemann, V. H., Ph.D. Thesis, University of Illinois, Urbana, IL, 1978.  
 (22) (a) Perry, S.; Zerda, T. W.; Jonas, *J. J. Chem. Phys.* **1981**, *75*, 4214. (b) Zerda, T. W.; Perry, S.; Jonas, *J. Ibid.* **1982**, *76*, 5774.  
 (23) Jonas, J.; Hasha, D. L.; Huang, S. G. *J. Chem. Phys.* **1979**, *71*, 3996.  
 (24) (a) Parkhurst, H. G., Jr.; Jonas, *J. J. Chem. Phys.* **1975**, *63*, 2698, 2705. (b) Tanabe, K.; Jonas, *J. Chem. Phys. Lett.* **1978**, *53*, 278.  
 (25) (a) Assink, R. A.; Jonas, *J. J. Chem. Phys.* **1972**, *57*, 3329. (b) DeZwaan, J.; Finney, R. J.; Jonas, *J. Ibid.* **1974**, *60*, 3223.  
 (26) Tanabe, K.; Jonas, *J. J. Chem. Phys.* **1977**, *67*, 4222.  
 (27) Assink, R. A.; DeZwaan, J.; Jonas, *J. J. Chem. Phys.* **1972**, *56*, 4975.  
 (28) (a) Finney, R. J.; Wolfe, M.; Jonas, *J. J. Chem. Phys.* **1977**, *67*, 4004. (b) Perry, S.; Schiemann, V. H.; Wolfe, M.; Jonas, *J. J. Phys. Chem.* **1981**, *85*, 2805.  
 (29) Wolfe, M.; Arndt, E.; Jonas, *J. J. Chem. Phys.* **1977**, *67*, 4012.  
 (30) (a) DeZwaan, J.; Jonas, *J. J. Chem. Phys.* **1975**, *63*, 4606. (b) Zerda, T. W.; Schroeder, J.; Jonas, *J. Ibid.* **1981**, *75*, 1612.  
 (31) (a) Jonas, J.; DeFries, T.; Wilbur, D. J. *J. Chem. Phys.* **1976**, *65*, 582. (b) DeFries, T.; Jonas, *J. Ibid.* **1977**, *66*, 896. (c) Lamb, W. J.; Jonas, *J. Ibid.* **1981**, *74*, 913. (d) Lamb, W. J.; Hoffman, G. A.; Jonas, *J. Ibid.* **1981**, *74*, 6875.  
 (32) (a) Finney, R. J.; Fury, M.; Jonas, *J. J. Chem. Phys.* **1977**, *66*, 760. (b) Jonas, J.; Perry, S.; Schroeder, J. *Ibid.* **1980**, *72*, 772.  
 (33) (a) Lee, Y.; Jonas, *J. J. Chem. Phys.* **1972**, *57*, 4233. (b) Wilbur, D. J.; DeFries, T.; Jonas, *J. Ibid.* **1976**, *65*, 1783. (c) DeFries, T.; Jonas, *J. Ibid.* **1977**, *66*, 5393.  
 (34) DeZwaan, J.; Jonas, *J. J. Chem. Phys.* **1975**, *62*, 4036.  
 (35) Perry, S. Ph.D. Thesis, University of Illinois, Urbana, IL, 1981.  
 (36) (a) Bull, T. E.; Jonas, *J. J. Chem. Phys.* **1970**, *52*, 2779. (b) Schindler, W.; Jonas, *J. Chem. Phys. Lett.* **1979**, *67*, 428. (c) Schindler, W.; Sharko, P. T.; Jonas, *J. J. Chem. Phys.* **1982**, *76*, 3493.  
 (37) Schindler, W.; Jonas, *J. unpublished results*.  
 (38) (a) Schindler, W.; Jonas, *J. J. Chem. Phys.* **1980**, *72*, 5019. (b) Schindler, W.; Jonas, *J. Ibid.* **1980**, *73*, 3547.  
 (39) Hasha, D. L., Ph.D. Thesis, University of Illinois, Urbana, IL, 1981.

of laser Raman scattering studies of various liquids. Reorientational motions and vibrational dephasing were the two main dynamic processes studied. Another problem of interest was the applicability of hydrodynamic equations at the molecular level, including the validity and applicability of the Stokes-Einstein<sup>9,46,47</sup> and the Debye<sup>48-52</sup> equations.

### Conformational Isomerization in Liquid Cyclohexane

In view of the importance of high-resolution NMR spectroscopy in diverse areas of chemistry, it is clear that high-resolution NMR of liquids at high pressure represents a promising new research field. The recent technological progress in the manufacture of superconducting magnets allowed construction of NMR probes capable of yielding high-resolution spectra of liquids at high pressure even without sample spinning.

As an example of one such application of this technique, I shall discuss some of our work<sup>1</sup> on the pressure effects on ring inversion of cyclohexane in several solvents. In addition to the simple goal of investigating the pressure effects on conformational isomerization, the main motivation of our study was to provide the first test of the predictions of the stochastic models for isomerization reactions.

- (40) Wolfe, M.; Jonas, *J. J. Chem. Phys.* **1979**, *71*, 3252.  
 (41) Jonas, J.; Arndt, E. *J. Magn. Reson.* **1978**, *32*, 297.  
 (42) Arndt, E.; Jonas, *J. J. Phys. Chem.* **1981**, *85*, 463.  
 (43) Lee, Y.; Jonas, *J. J. Chem. Phys.* **1973**, *59*, 4845.  
 (44) Jonas, J.; Hasha, D. L.; Huang, S. G. *J. Phys. Chem.* **1980**, *84*, 109.  
 (45) (a) Lee, Y.; Jonas, *J. J. Magn. Reson.* **1971**, *5*, 267. (b) Lee, Y.; Campbell, J. H.; Jonas, *J. J. Chem. Phys.* **1974**, *60*, 3537. (c) Akai, J. A.; Jonas, *J. J. Solution Chem.* **1976**, *5*, 563.  
 (46) (a) Alder, B. J.; Alley, W. E.; Rigby, M. *Physica (Utrecht)* **1974**, *73*, 143. (b) Alley, W. E.; Alder, B. J. *J. Chem. Phys.* **1975**, *63*, 3764.  
 (47) Hynes, J. T. *Annu. Rev. Phys. Chem.* **1977**, *28*, 301.  
 (48) Kivelson, D.; Kivelson, M. G.; Oppenheim, I. *J. Chem. Phys.* **1970**, *52*, 1810.  
 (49) Bauer, D. R.; Brauman, J. I.; Pecora, R. *J. Am. Chem. Soc.* **1974**, *96*, 6840.  
 (50) Hu, C. M.; Zwanzig, R. *J. Chem. Phys.* **1974**, *60*, 4354.  
 (51) Fury, M.; Jonas, *J. J. Chem. Phys.* **1976**, *65*, 2206.  
 (52) Hynes, J. T.; Kapral, R.; Weinberg, M. *J. Chem. Phys.* **1978**, *69*, 2725.

In order to make clear the significance of our NMR experimental results, I have to introduce the main features of the stochastic models for isomerization reactions. These models predict the existence of dynamic effects on isomerization reactions because the reaction coordinate is expected to be coupled to the surrounding medium. In contrast to classical transition theory<sup>53</sup> (TST) where the transmission coefficient  $\kappa$  is assumed to be unity and independent of the thermodynamic state, the stochastic models<sup>54-58</sup> propose that  $\kappa$  is dependent on the "collision frequency",  $\alpha$ , which in the absence of electrostatic effects reflects the actual coupling of the reaction coordinate to the surrounding medium. The stochastic models introduce<sup>57,58</sup>  $\kappa$  as

$$k(\Delta t) = \kappa k_{\text{tst}} \quad (1)$$

where  $k(\Delta t)$  is the observed isomerization rate and  $k_{\text{tst}}$  represents the reaction rate as defined in the classical transition-state theory. Then it follows that

$$\Delta V_{\text{obsd}}^* = \Delta V_{\text{coll}}^* + \Delta V_{\text{tst}}^* \quad (2)$$

where  $\Delta V_{\text{obsd}}^*$  is the observed activation volume,  $\Delta V_{\text{coll}}^*$  is the collision contribution to the activation volume defined as

$$\Delta V_{\text{coll}}^* = -RT(\partial \ln \kappa / \partial P)_T \quad (3)$$

and  $\Delta V_{\text{tst}}^*$  is the transition-state activation volume. According to the stochastic model, one would expect a large pressure dependence of  $\Delta V_{\text{coll}}^*$  because  $\kappa$  is a strong function of the collisional frequency  $\alpha$ . The theory predicts that with weak coupling an increase in pressure will lead to an increase in the isomerization rate, whereas with strong coupling an increase in pressure will decrease the isomerization rate. There is a nonmonotonic transition between the weak and strong coupling regimes.

We selected cyclohexane for our study for several reasons. First, cyclohexane has no dipole moment and the coupling to the surrounding medium is given by the collision frequency,  $\alpha$ , which is approximately proportional to the shear viscosity,  $\eta$ , of the solvent. Second, the ring inversion in cyclohexane is a relatively simple process, such that to a first approximation one can compare the experimental results with the predictions of the stochastic models on the basis of a one-dimensional bistable potential.

Because one can relate  $\alpha$  to viscosity,  $\eta$ , of the medium by using simple hydrodynamic arguments, one can select different solvents in order to cover the various regions of the  $\kappa$  vs.  $\alpha$  dependence. Acetone- $d_6$ , carbon disulfide, and methylcyclohexane were selected. Using standard line shape analysis, we studied the pressure dependence of ring inversion of cyclohexane at several temperatures in these three solvents.

In our experiments we found that, as predicted by the stochastic models, the  $\Delta V_{\text{obsd}}^*$  was strongly pressure and solvent dependent as were the collisional contributions to the activation volume  $\Delta V_{\text{coll}}^*$ . Our results are shown

(53) Glasstone, S.; Laidler, K. J.; Eyring, H. "Theory of Rate Processes"; McGraw-Hill: New York, 1941.

(54) Kramers, H. A. *Physica (Amsterdam)* 1940, 7, 284.

(55) Lassier, B.; Brot, C. *Discuss. Faraday Soc.* 1969, 48, 39.

(56) Troe, J. In "High Pressure Chemistry"; Kelm, H., Ed.; D. Reidel: Dordrecht, Holland, 1978; pp 489-520.

(57) Skinner, J. L.; Wolynes, P. G. *J. Chem. Phys.* 1978, 69, 2143.

(58) Montgomery, J. A.; Chandler, D.; Berne, B. J. *J. Chem. Phys.* 1979, 70, 405.

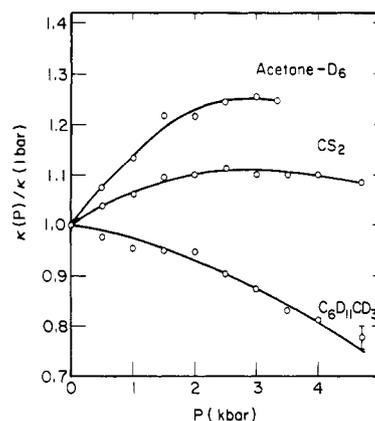


Figure 3. Pressure dependence of the reduced transmission coefficient,  $\kappa$ , for conformational isomerization of cyclohexane in several solvents (indicated in the figure).

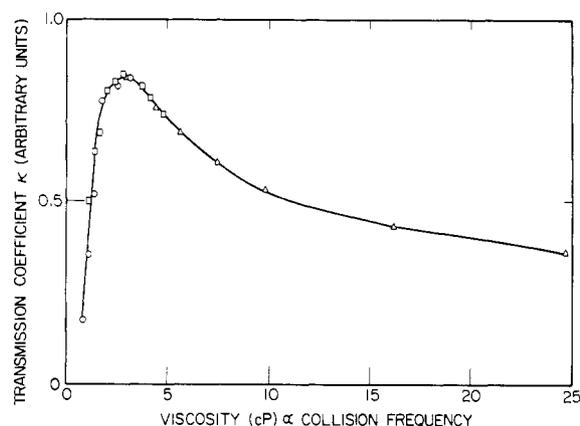


Figure 4. Relation between the transmission coefficient  $\kappa$  (given in arbitrary units) and viscosity (proportional to collisional frequency  $\alpha$ ), for conformational isomerization of cyclohexane at 225 K. Solvents: (O) acetone- $d_6$ , (□) carbon disulfide, and (Δ) methylcyclohexane- $d_{14}$ .

in Figure 3, which gives the reduced transmission coefficient  $\kappa(P)/\kappa(1 \text{ bar})$  as a function of pressure,  $P$ , for the three solvents studied. In acetone- $d_6$ ,  $\kappa$  increased by 30% of its initial value at 1 bar and leveled off at about 2.5 kbar. In carbon disulfide,  $\kappa$  initially increased but only by about 10% and then decreased slightly at the highest pressures. In contrast,  $\kappa$  in cyclohexane- $d_{12}$  showed an 80% decrease from its initial value at 1 bar. From these results we readily see that in the acetone and  $\text{CS}_2$  solvents  $\kappa$  is in the weak coupling region ( $\kappa$  proportional to  $\alpha$ ), whereas in deuterated cyclohexane  $\kappa$  is in the strong coupling region ( $\kappa \propto 1/\alpha$ ). An even better representation of the experimental results is given in Figure 4, which shows the dependence of the reduced transmission coefficient upon the solvent viscosity,  $\eta$ . As predicted by the stochastic models,  $\kappa$  shows a nonmonotonic dependence upon  $\eta$  (approximately proportional to the collision frequency  $\alpha$ ) and indicates the weak and strong coupling regions. Our results provide the first experimental demonstration of the theoretical predictions of the stochastic models. Several additional promising applications of this high-resolution high-pressure NMR technique will be mentioned in the concluding remarks.

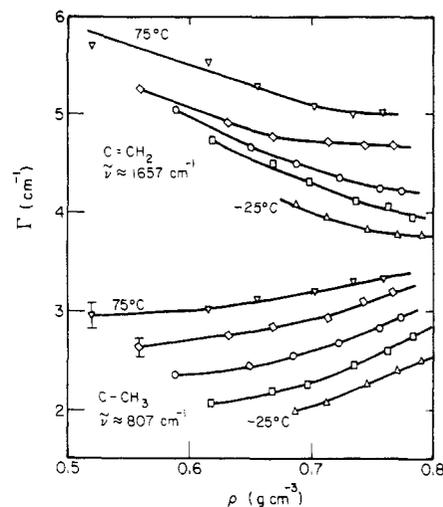
### Raman Studies of Vibrational Dephasing

Before presenting our results of Raman studies, it is necessary to discuss very briefly the Raman scattering

experiments and the unique information about reorientational and vibrational processes in liquids that they provide. From the experimental polarized and depolarized Raman bandshapes, one can obtain<sup>59</sup> the isotropic scattering intensity,  $I_{\text{iso}}(\omega)$ , and the anisotropic scattering intensity,  $I_{\text{aniso}}(\omega)$ . Only vibrational (nonorientational) processes contribute to  $I_{\text{iso}}(\omega)$ , whereas both reorientational and vibrational processes contribute to  $I_{\text{aniso}}(\omega)$ . This provides the means of separating reorientational processes from vibrational processes and of calculating reorientational and vibrational correlation functions.

The broadening of isotropic Raman bandshapes may be influenced by several mechanisms. The two dominant ones involve energy relaxation via inelastic collision and phase relaxation via quasielastic collisional processes. Both mechanisms have been investigated,<sup>60</sup> and it has been found that phase relaxation (dephasing) in liquids always occurs much faster than energy relaxation. In all the cases discussed in this section, the broadening of the isotropic Raman line shapes arises from a dephasing process. Many different theories dealing with dephasing have recently been developed (for review, see ref 60), examples of which are the isolated binary collision (IBC) model,<sup>61,62</sup> the hydrodynamic model,<sup>63</sup> the cell model,<sup>64</sup> and the model based on resonant energy transfer.<sup>65</sup>

In the measurements of isotropic line shapes of the C-H, C-D, and C-C stretching modes in a variety of simple molecular liquids (see Table I), we found that the IBC model,<sup>61,62</sup> which considers only the repulsive part of the intermolecular potential in calculating the dephasing rate, reproduces the general trends of the experimental data observed. I should point out that this model and other models predict that the dephasing rate (line width) will increase with density at constant temperature; therefore, it was interesting to observe a very different behavior of the dephasing rate in liquid isobutylene.<sup>38</sup> The Raman line shapes of the  $\nu_4(A_1)$  symmetry C=CH<sub>2</sub> stretching mode of 1657 cm<sup>-1</sup> and the  $\nu_9(A_1)$  symmetric C-CH<sub>3</sub> stretching mode of 805 cm<sup>-1</sup> in isobutylene were measured as a function of pressure from vapor pressure to 0.8 g cm<sup>-3</sup>, over the temperature range from -25 to 75 °C. Figure 5 shows the density dependence of the experimental half width  $\Gamma = (2\pi c\tau_v)^{-1}$ , where  $\tau_v$  is the dephasing time and  $\Gamma$  is proportional to the dephasing rate. From Figure 5 we see that increasing density, at constant temperature, affects the bandwidths of the two vibrations in a qualitatively different way. The C-CH<sub>3</sub> stretching bandwidth increases with increasing density, a behavior found for many other modes of liquids. This basic trend can be predicted in terms of a IBC model<sup>61,62</sup> based on rapidly varying repulsive interactions. The most interesting result of this study was the observed decrease of the bandwidth of the C=CH<sub>2</sub> stretching mode (strongly infrared active band) with increasing density. To my best knowledge, this was the first experimental observation of a decrease in dephasing rate



**Figure 5.** Density dependence of the half-width at half-maximum intensity,  $\Gamma$  (cm<sup>-1</sup>), for the C=CH<sub>2</sub> and the C-CH<sub>3</sub> stretching modes in liquid isobutylene, over the temperature range from -25 to 75 °C.

with increasing density in liquid. It appears that this band is inhomogeneously broadened as it is affected by environmentally induced frequency fluctuations. These fluctuations are due to dispersion, induction, and electrostatic forces that depend on the dipole (0.5 D) and polarizability of the molecule. The decay of the inhomogeneous environment around a molecule results in motional narrowing. The correlation function modeling,<sup>66</sup> which uses the Kubo stochastic lineshape theory,<sup>67</sup> was in agreement with our experimental data. In further studies we found a similar decrease in bandwidth for the C=O stretching mode in liquid acetone.<sup>36</sup> Again, the attractive interactions influence the dephasing process and are responsible for the density behavior of the bandwidth.

The Raman experiments on isobutylene and acetone have been discussed in a theoretical study of dephasing by Schweizer and Chandler,<sup>68</sup> who analyzed in detail the relative role of slowly varying attractive interactions and rapidly varying repulsive interactions on the frequency shifts and dephasing in liquids. Their theoretical model correctly predicts the isothermal density dependence of the C=CH<sub>2</sub> bandwidth in isobutylene and the C=O bandwidth in acetone. In this connection it is useful to mention that we found a very different density dependence for the frequency shifts of these two vibrational modes in isobutylene.<sup>38</sup> From the experimental data it is clear that the isothermal density dependence of frequency shifts provides very useful information about the nature of intermolecular interactions<sup>68</sup> in liquids and reflects the relative effects of the attractive and repulsive forces. As an illustration, Figure 6 shows the frequency shifts of the C=CH<sub>2</sub> and C-CH<sub>3</sub> modes in liquid isobutylene as a function of density.

### Collision-Induced Raman Scattering

Until recently our work focused on the investigation of the properties of individual molecules such as reorientational or vibrational dephasing, which reflect

(59) Nafie, L. A.; Peticolas, W. L. *J. Chem. Phys.* **1972**, *57*, 3145.

(60) Oxtoby, D. W. *Annu. Rev. Phys. Chem.* **1981**, *32*, 77.

(61) Fischer, S. F.; Laubereau, A. *Chem. Phys. Lett.* **1975**, *35*, 6.

(62) Oxtoby, D. W.; Rice, S. A. *Chem. Phys. Lett.* **1976**, *42*, 1.

(63) Oxtoby, D. W. *J. Chem. Phys.* **1979**, *70*, 2605.

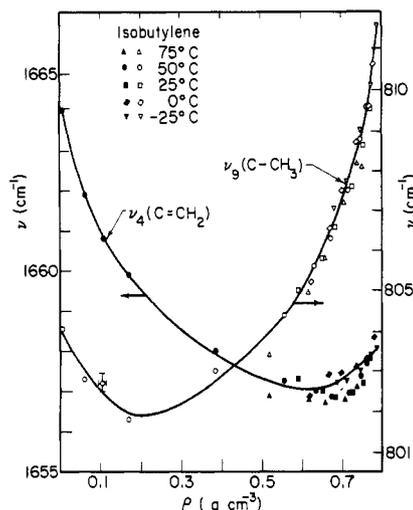
(64) Diestler, D. J.; Manz, J. *Mol. Phys.* **1977**, *33*, 227.

(65) Doge, D. Z. *Naturforsch.*, **1973**, *28*, 919.

(66) Rothschild, W. G. *J. Chem. Phys.* **1976**, *65*, 455.

(67) Kubo, R. In "Fluctuations, Relaxation, and Resonance in Magnetic Systems"; Ter Haar, D., Ed.; Plenum Press: New York, 1962.

(68) Schweizer, K. S.; Chandler, D. *J. Chem. Phys.* **1982**, *76*, 1128.

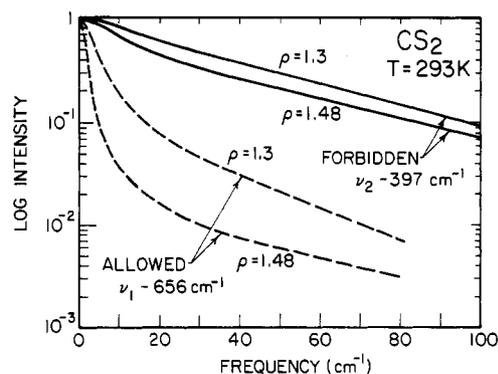


**Figure 6.** Density dependence of the isotropic band frequency for the C=CH<sub>2</sub> and the C-CH<sub>3</sub> stretching modes in liquid isobutylene.

only indirectly the influence of intermolecular interactions. However, studies of collision-induced (interaction induced) spectra<sup>67,70</sup> can provide direct information about intermolecular interactions by investigating the interaction-induced forbidden Raman bands and the interaction-induced wings for allowed Raman bands. I shall mention briefly some of the results obtained in our laboratory because, again, in this specific area the investigation of density effects is essential.

The second rotational moment,  $M_R(2)$ , is related to the rotational kinetic energy of the molecule and should not change with density. Its value is constant at a given temperature,  $M_R(2) = 6kT/I \ll \langle \text{prop} (I_{\perp}) \rangle$  ( $I_{\perp}$  is the molecular moment of inertia perpendicular to the symmetry axis). In contrast to this prediction we found that  $M_R(2)$  is strongly density dependent in liquid chloroform<sup>3</sup> and propyne.<sup>4</sup> In these cases we found that  $M_R(2)$  decreases with increasing density.

For example, for the  $\nu_1(A_1)$  C-H stretching mode in liquid chloroform<sup>3</sup> at 303 K, there is a decrease from 510 to 223 cm<sup>-2</sup> with a density increase from 1.47 to 1.78 g cm<sup>-3</sup> ( $6kT/I_{\perp} = 278$  cm<sup>-2</sup> at 303 K). The decrease of the second moment with increasing density can be explained in terms of collision-induced scattering (CIS) that contributed to the wings of the Raman band. The fact that the CIS affects only the far wings of the band explains why this effect was very often neglected; the correlation functions and the correlation times are affected only slightly. However, second moment analysis, which describes the short-time behavior of a correlation function and thus reflects the collision-induced high-frequency contributions to the spectral line rather strongly, is the most reliable method of investigating short-time intermolecular interactions. The reason why the second moment decreases with increasing density is related to the decrease of collision-induced scattering with increasing density. Clearly, dynamic effects are not as inefficient over short-time intervals as had been previously assumed. Evidently, three- and four-particle correlations must be included in any description of the scattering process. In their molecular dynamics calcu-



**Figure 7.** Density effects on the intensity profile for the allowed  $\nu_1$  (656 cm<sup>-1</sup>) band and the forbidden  $\nu_2$  (397 cm<sup>-1</sup>) band in liquid CS<sub>2</sub> at 293 K.

lations, Alder et al.<sup>71</sup> investigated the effects of density on bands of depolarized light scattering from atomic fluids, taking into account not only two-particle but also three- and four-particle correlations. At low densities the pairwise term dominates and increases with density, whereas at higher densities cancellations occur between the pairwise, triplet, and quadruplet terms with the result that the total scattering intensity decreases. We proposed<sup>3,4</sup> that an analogous process is responsible for the decrease of CIS with increasing density in our liquid studies.

In our preliminary experiments<sup>72</sup> dealing with the density effects on interaction-induced spectra in simple molecular liquids such as the triatomics, CS<sub>2</sub> and COS, we found that density affects in a major way the intermolecular interactions and changes the CIS. Figure 7 illustrates the density effects on the CIS for allowed and forbidden bands in liquid CS<sub>2</sub>.

This figure shows the logarithmic plot of intensity vs. frequency for the allowed  $\nu_1$  (656 cm<sup>-1</sup>) band and the forbidden  $\nu_2$  (397 cm<sup>-1</sup>) band in liquid CS<sub>2</sub> at two densities. It is evident that the increase in density has a pronounced effect both on the far-wing CIS contribution to the allowed band and on the forbidden band.

### Concluding Remarks

From the specific examples discussed above it is evident that pressure is an essential experimental variable in studies of dynamic processes in liquids. This conclusion is of general validity and applies to all experimental techniques used to investigate the structure and dynamics of liquids. Current developments in various experimental techniques and in high-pressure instrumentation make such high-pressure experiments possible. Complete isobaric, isothermal, and isochoric data are essential for a rigorous test of various theoretical models of liquids or for establishing a sound experimental basis in developing new theoretical models.

In the NMR field one can expect multinuclear high-resolution NMR spectroscopy at high pressures to have a significant impact in several areas of chemistry. First, studies dealing with various exchange processes of the type discussed for the cyclohexane ring inversion will provide new information about isomerization and other reactions occurring in the liquid state. Second, one can

(69) Birnbaum, G. In "Vibrational Spectroscopy of Molecular Liquids and Solids"; Bratos, S., Pick, R. M., Ed.; Plenum Press: New York, 1980.

(70) Madden, P. A. In "Raman Spectroscopy—Linear and Nonlinear"; Lascombe, J., Huang, P. V., Ed.; Wiley: New York, 1982.

(71) (a) Alder, B. J.; Weiss, J. J.; Strauss, M. L. *Phys. Rev.* **1973**, *47*, 281. (b) Alder, B. J.; Strauss, H. L.; Weiss, J. J. *J. Chem. Phys.* **1973**, *59*, 1002.

(72) Hegemann, B.; Jonas, J., unpublished results.

also predict important activity in the area of biochemical applications. For example, the problem of pressure denaturation of proteins as investigated by Weber and Drickamer<sup>73</sup> could be studied by the high-resolution NMR technique. Third, on the basis of the studies<sup>74</sup> performed in our laboratory, one can foresee a bright future of this technique in the field of homogeneous catalytic processes.

As far as Raman scattering studies of liquids are concerned, there is a definite need for additional systematic studies of reorientational motions, vibrational dephasing, and frequency shifts in various fluids. The information content of temperature and density effects on frequency shifts of various vibrational bands has not

yet been fully explored. In particular, the frequency difference<sup>36,75</sup> found between the polarized and depolarized bands in dipolar fluids will offer new information about strong dipolar interactions in liquids.

The problem of collision-induced scattering in polyatomic molecular fluids can only be attacked by using high-pressure techniques. Since this novel research area offers direct information about intermolecular interactions in liquids, an increasing activity in studies of collision-induced scattering in liquids can be expected.

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(73) Weber, G.; Drickamer, H. G., *Q. Rev. Biophys.*, in press.

(74) (a) Heaton, B. T.; Jonas, J.; Eguchi, T.; Hoffman, G. A. *J. Chem. Soc., Chem. Commun.* 1981, 331. (b) Heaton, B. T.; Strona, L.; Jonas, J.; Eguchi, T.; Hoffman, G. A. *J. Chem. Soc., Dalton Trans.* 1982, 1159.

(75) (a) Fini, G.; Mirone, P.; Fortunato, B. *J. Chem. Soc., Faraday Trans.* 1973, 269, 1243. (b) Fini, G.; Mirone, P. *J. Chem. Soc., Faraday Trans.* 1974, 270, 1776. (c) Fini, G.; Mirone, P. *Spectrochim. Acta, Part A* 1976, 32, 625.