Spectroscopic Studies of Molecular Motion in Liquids[1]

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A knowledge of vibrational, rotational, and translational motions of molecules in liquids can provide a valuable insight into the dynamics of the liquid state. It has been possible, in the past several years, through infrared and Raman studies of simple liquids to learn about these molecular motions. The results of some of these investigations will be presented here. This type of information shows promise as an aid in the development and evaluation of useful models of the liquid state.

Infrared and Raman spectra of gas-phase molecules can determine vibrational energies of molecules and, from the fine structure of the band, rotational energies can be established. Since translational energies form a continuum in the gas phase, these are detected only indirectly from the broadening of rotational fine structure.

In the liquid phase vibrational energy level spacings are shifted only slightly since the potential energies of intermolecular interactions are orders of magnitude smaller than the potentials associated with the vibrating chemical bond. Translational and rotational motions, on the other hand, are greatly changed by the liquid environment. For dilute gases, free translation can occur over many molecular diameters before being deflected by a collision. In the liquid state, translation is best described by a rattling or diffusive motion since each molecule is trapped in a cavity formed by neighboring molecules. For light molecules confined to their small solvent cages, the translational frequencies can be high enough so that they can be investigated directly by spectroscopy. Whereas rotation is free in the gas phase, except for the brief duration of a collision, this motion can become interrupted and hindered by the angularly dependent potentials of the molecule with its neighbors in the liquid. Since the spacings of rotational levels (except for H_2) are smaller than the intermolecular potentials, these levels are greatly perturbed. Moreover the frequent collisions in the liquid which can relax rotational states cause broadening. Expressed in classical terms, since translational frequencies in the liquid are usually comparable to rotational frequencies, these motions become easily coupled. The result of these interactions is to smear out individual rotational fine structure. Information on the rotational motion is, however, contained in the band shape.

In the present discussion the determination of rotational and translational motions by infrared and Raman spectroscopy in (nonmetallic, nonionic) liquids will be described. Since solvent shifts of vibrational levels are discussed elsewhere,[2] these will not be considered here. A comprehensive review by Robin[3] on spectroscopy of simple liquids, which considers in addition to infrared and Raman results a discussion of electronic transitions, has recently appeared.

Rotational Motion

The first convincing evidence that quantized rotational energy levels can exist in the liquid state was provided by McLennan and McLeod,[4] who observed discrete rotational transitions in the Raman spectrum of liquid hydrogen in 1929. A number of infrared studies of H_2 and its isotopes in the pure liquids[5] and in solutions[6] have been made since that time. As a recent example of these types of spectroscopic investigations consider the far-infrared study of a dilute solution of H_2 in liquid argon by Holleman and Ewing[7] shown in Figure 1. The observed absorption is a result of the molecular quadrupole moment of H_2 which induces a dipole in the surrounding liquid environment. Since this induced dipole moment is modulated as H_2 rotates and translates in the liquid state, transitions involving changes in these energies are made allowed in the far-infared.[8] The sharp features in Figure 1 are assigned to transitions in which H_2 changes its rotational quantum state from $J = 2 \leftarrow J = 0$ or $J = 3 \leftarrow J = 1$. The frequencies of these transitions do not differ from those calculated for the unperturbed gas-phase molecule within the experimental error (<2 cm^{-1}). Similar rotational transitions observed in a D_2–argon solution have frequencies which also agree with gas-phase values. *The conclusion is that H_2 and D_2 are free rotors in this liquid-state system.* From band-width measurements the barrier to rotation for H_2 in liquid argon must be less than 25 cm^{-1} (70 cal/mol), which is much smaller than the separation of 120 cm^{-1} between the lowest rotational states.

Spectroscopic studies have revealed discrete rota-

(1) Contribution No. 1663 from the Chemical Laboratories of Indiana University. Supported by a grant from the National Science Foundation.

(2) A. D. Buckingham, *Proc. Roy. Soc.*, (London), **A248**, 169 (1958).

(3) H. L. Frisch and Z. Salsburg, "Simple Dense Fluids," Academic Press, New York, N. Y., 1968; see especially pp 217–247.

(4) J. McLennan and J. McLeod, *Nature*, **123**, 160 (1929).

(5) E. Allen, T. Feldman, and H. Welsh, *J. Chem. Phys.*, **24**, 1116 (1956); H. Gush, W. Hare, E. Allen, and H. Welsh, *Can. J. Phys.*, **38**, 176 (1960).

(6) (a) M. O. Bulanin, and N. Orlova, *Opt. Spectry.*, **11**, 298 (1961); (b) G. Ewing and S. Trajmar, *J. Chem. Phys.*, **42**, 4038 (1965).

(7) G. Holleman and G. Ewing, *ibid.*, **47**, 571 (1967).

(8) J. Van Kranendonk, *Physica*, **23**, 825 (1957); **24**, 347 (1958); **25**, 337 (1959).

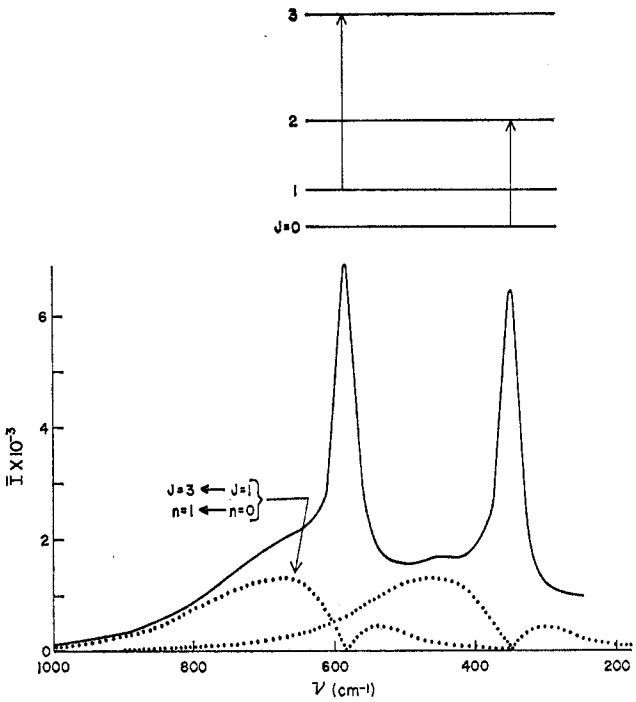

Figure 1. Rotation–translation spectrum of H_2 in liquid argon. The H_2 concentration is 1 mol % and the solution temperature is 87°K. The absorption is given by $\bar{I} = 1/\nu \ln (T_0/T)$. The energy level diagram above the spectrum indicates the pure rotational transitions of H_2. The solid curve is the experimental absorption. The dotted curve, a result of a profile analysis, shows the contribution of translational fine structure to the rotational transitions [G. Holleman and G. Ewing, *J. Chem. Phys.*, **47**, 571 (1967)].

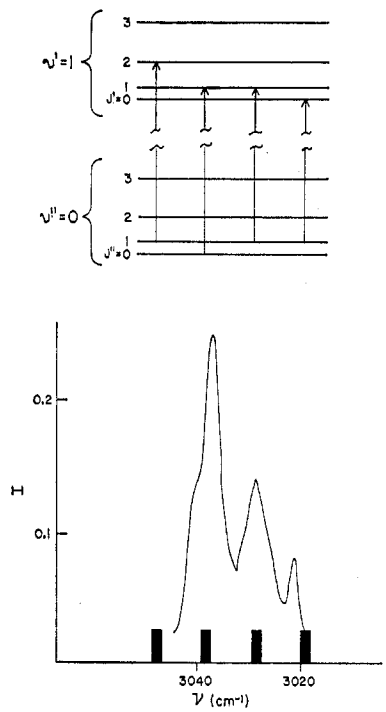

Figure 2. Infrared absorption spectrum of 0.2% CH_4 in solid argon at 4°K in the ν_3 region. The absorption is given by $I = \log (T_0/T)$. The energy level diagram above the spectrum indicates the vibration–rotation transitions allowed for the gas-phase molecule. The lines below the spectrum indicate the frequencies of the gas-phase transitions corrected for vibrational shift. Because of the complications of nuclear spin conversion, the relative intensities of these lines are arbitrarily taken to be equal [F. Frayer and G. Ewing, *J. Chem. Phys.*, **48**, 781 (1968)].

tional transitions in no liquid systems except those containing H_2 or its isotopes. Molecules which might be expected to undergo relatively unhindered rotation in the liquid state are those with weak intermolecular forces and large rotational separations (*e.g.*, N_2, O_2, HCl, CH_4, etc.). For an insight into the reason that no discrete rotational transitions are observed in these simple molecules, let us consider the simple example of methane. Since CH_4 is spherical, and its van der Waals interactions are small, its solution in argon might be expected to experience a small barrier to rotation. Before looking at the liquid system, however, let us first examine the solid solution.

The ν_3 infrared region of a dilute CH_4–Ar solid solution at 4°K by Frayer and Ewing[9] is given in Figure 2 together with an energy level diagram for the gas-phase molecule. The vertical lines in the figure indicate that, while there is qualitative agreement between the gas-phase energy levels and those observed in the solid solution, the rotation of CH_4 is not free. King has calculated the rotational energy level diagram for a rigid tetrahedron (CH_4) in a cubic field (solid argon) which has been reproduced in Figure 3.[10] The barrier is indicated by the dimensionless parameter β. Two values of β which fit the data equally well are 16.5 and −12. These relate respectively to the C–H bonds finding a minimum of energy pointing at the argon atoms or between them. The corresponding barrier heights are 1.5 or 1.1 kcal/mol. The first eight rotational levels are beneath the barrier, and CH_4 must therefore be considered a hindered rotor. This differs qualitatively from the H_2–liquid argon case just considered in which the barrier to rotation was much less than the rotational separation of even the lowest levels. Notice the involved splitting that occurs for the rotational levels for $J \geq 2$. Since the cavity size for CH_4 in liquid argon must be comparable to that in the solid, the barriers to rotation will also be of the same order of magnitude. The complications introduced by the liquid state are considerable. The site symmetry around CH_4 is not cubic but consists of a variety in the number of nearest neighbors and their configurations. This produces a distribution of barrier heights. The observed spectrum will reflect a superposition over the different "local environments"[11] of all the solute molecules, and the individual levels will be broadened out of recognition. Rapid fluctuations in these local environments (*i.e.*, collisions and diffusive motions of neighboring molecules) allow rotational relaxation which also contributes to the broad-

(9) F. Frayer and G. Ewing, *J. Chem. Phys.*, **48**, 781 (1968).
(10) H. F. King, private communication.
(11) J. Kwok and G. Robinson, *J. Chem. Phys.*, **36**, 3137 (1962).

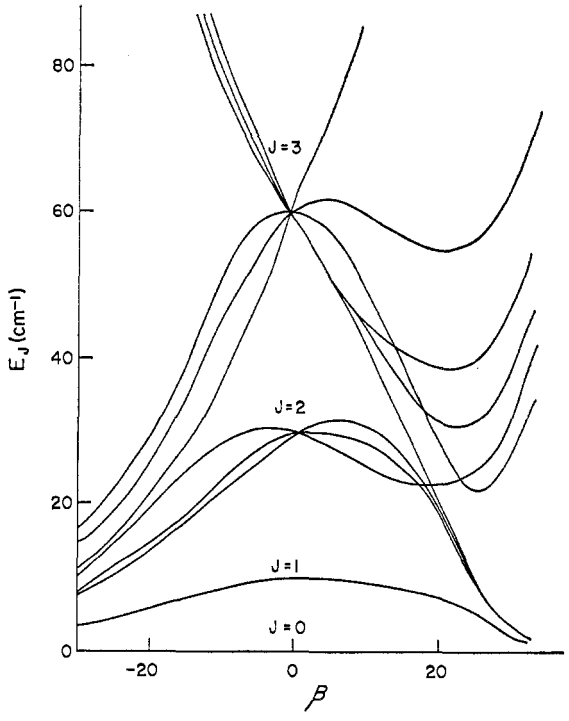

Figure 3. Rotational energy levels of a rigid tetrahedron (CH_4) in a cubic crystal lattice (Ar). The potential barrier is represented by the dimensionless parameter β (H. F. King, private communication).

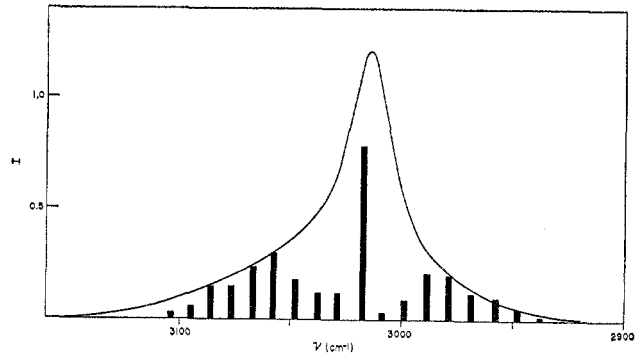

Figure 4. Infrared absorption of a 0.15% solution of methane in liquid argon at 100°K in the ν_3 region. The absorption is given by $I = \log (T_0/T)$. The vertical lines are calculated for the free rotor (A. Cabana, private communication).

ening. It is therefore no surprise that the infrared spectrum of CH_4 in liquid argon (Figure 4) shows no individual vibration–rotation transitions. A comparison of the band width with the theoretical gas-phase absorption strongly suggests that the band shape can be attributed to rotation. Studies of pure liquid CH_4 and CD_4 also reveal broad structureless absorption.[12] A significantly more narrow band width for CD_4 than for CH_4 is consistent with the interpretation that rotatory motion can account for the band shape. Raman work of Crawford, *et al.*,[13] on liquid methane also reveals very broad vibration–rotation band shapes.

The complex energy level diagram of Figure 3 together with the concept of fluctuating local environments suggests the hopelessness of the task of trying to discuss rotatory energy levels in the liquid state for molecules more complex than H_2 in terms of discrete states. Some attempts along these lines have been made, and while they can lend some physical insight into the possible effect of liquid environment on rotation, they have only been qualitatively successful in interpreting spectroscopic data.[14,15]

Gordon has suggested an exciting new approach to the understanding of these band shapes.[16] He shows that the Fourier transform of the infrared absorption yields the dipole correlation function

$$\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle = \int_{\text{band}} \hat{I}(\nu) \cos 2\pi\nu t \, d\nu$$

The band absorption, $\hat{I}(\nu)$ $(=I(\nu)/\int I(\nu)d\nu)$, is normalized to unit area and ν is measured relative to the center of the absorption. For a clear intuitive interpretation of the correlation function it is best to quote directly from Gordon: "The physical meaning of the correlation function $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$ (at least in the classical limit, where measurements do not disturb the system) is the following: Imagine that one could observe the microscopic reorientation of a single molecule in a system of many molecules in thermal equilibrium. Suppose that at a time 0 the vibrating dipole of this molecule points along a direction $\hat{\mu}(0)$. Then we follow the thermal motion of the molecules and at a time later we measure the projection of $\hat{\mu}(t)$ on the original direction: $\hat{\mu}(0) \cdot \hat{\mu}(t)$. Now we make this measurement again and again, picking out a different reference time "0." Finally, we average all of these trajectories $\hat{\mu}(0) \cdot \hat{\mu}(t)$ to obtain the correlation function $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$. A slightly different way to view this correlation function is to say that it describes the decay of our knowledge about a system as it approaches equilibrium. Even if we know that a molecule points in a certain direction at time $t = 0$, after a long time it is equally likely to be pointing in any direction. Then our initial knowledge is no longer relevant. The correlation function is a quantitative statement of what average predictions may be made after a given time, using our initial knowledge."[16]

Let us now consider a dipole correlation analysis on the solution spectrum of CH_4 in liquid argon. Bardoux, *et al.*,[17] have transformed the infrared spectra shown in Figure 4 to obtain $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$ and the results are presented in Figure 5. At $t = 0$ the dipoles have not moved from their initial positions and $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle = 1$. For $t < 0.3 \times 10^{-12}$ sec, the dipole correlation func-

(12) G. Ewing, *J. Chem. Phys.*, **40**, 179 (1964).
(13) M. Crawford, H. Welsh, and J. Harrold, *Can. J. Phys.*, **30**, 81 (1952).
(14) G. Ewing, *J. Chem. Phys.*, **37**, 2250 (1962).
(15) D. Robert and L. Galatry, *Chem. Phys. Letters*, **1**, 399, 526 (1968).
(16) R. Gordon, *J. Chem. Phys.*, **39**, 2788 (1963); **41**, 1819 (1964); **43**, 1307 (1965).
(17) R. Bardoux, A. Chamberland, and A. Cabana, Symposium on Molecular Structure and Spectroscopy, 1968, Paper U1.

tion is curved but lies above that for a classical free rotor (dashed curve). The experimental dipole correlation function therefore decays more slowly than for a free rotor. Physically this means that intermolecular torques in the liquid cause the dipole directions to change more slowly than in the free molecule. The correlation function for $t \gtrsim 0.3 \times 10^{-12}$ sec decays exponentially to zero. This is consistent with the nature of a stochastic process in which the dipoles undergoing hindered rotation are interrupted so many times by fluctuations in the liquid that their orientations are becoming completely randomized.

The results of this analysis of liquid methane solutions is consistent with the high hindering barriers determined from the solid solution study[9] together with the fluctuations of these barriers expected for the liquid environment. The methane results are probably typical of most molecular systems [except H_2] since the barrier height is expected to be greater than the rotational spacings. It is therefore understandable that no rotational fine structure has been observed in liquid spectra [except H_2] even though a fairly large number of small molecules have been investigated.

There are several problems in treating spectroscopic data to obtain correlation functions that should be mentioned. Serious errors can arise in connection with Fourier transforms due to finite data truncation so that high resolution spectral information over the band and out into the "wings" is required. In studies of pure liquids, thin films required may approach thicknesses of dimension comparable to the wavelength of light used for the absorption measurements and this may result in distortion of the band shape. For this reason ATR measurements have been applied to obtain correlation functions.[18] Another problem is that the effects of induced absorption are not included in the present theory. In cases where the induced absorption is believed to contribute significantly to the observed spectrum it must be subtracted out before the correlation function is calculated. Such a correction has recently been applied to the rotational spectrum of hydrogen halides in cyclohexane.[19] Fluctuations in the vibrational frequency shift may produce band broadening that would lead to erroneous correlation functions.[16]

Dipole correlation analysis of pure liquid CH_4, CO,[16] and larger molecules[18,20] indicates the same qualitative behavior shown in Figure 5. A rotatory motion can be considered uninterrupted but hindered for times short compared to that for a free rotation. For longer times the rotation is randomized by the frequent environmental changes in the liquid media. A discussion of time-correlation functions determined from spectral band shapes in terms of models of molecular

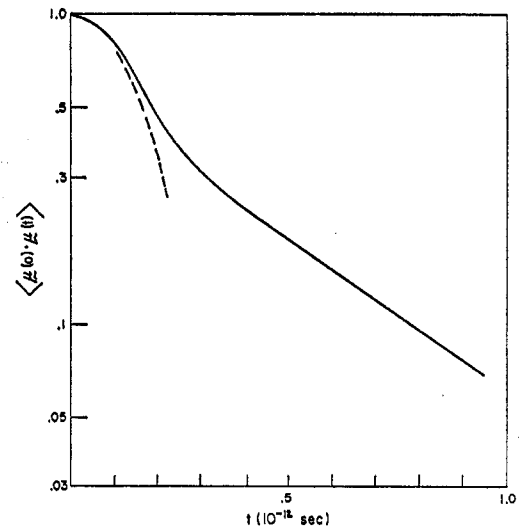

Figure 5. Dipole correlation function for methane in liquid argon computed from infrared data of Figure 4. The dashed curve represents the classical correlation function for a free rotor (A. Cabana, private communication).

reorientation in liquids is given by Shimizu[21] and Gordon.[16]

Spectroscopic evidence for rotational motions of other small molecules in the liquid state without recourse to a dipole correlation analysis is available from other studies. Datta and Barrow[22] investigated the far-infrared spectrum of hydrogen halides in inert solvents and observed a broad absorption which qualitatively agrees with the unresolved rotational envelope calculated for a rotating HCl molecule. The vibrational spectra of HCl in various solvents also suggest rotational motion since the band contours resemble an unresolved P, Q, and R branch.[23] Raman studies of liquid O_2 and N_2 reveal vibrational band shapes which suggest unresolved S, Q, and O branches.[13]

The band shape of the Rayleigh wings of light scattered from CS_2 in liquids has been measured by Shapiro and Broida.[24] These contours do not resemble rotational band shapes and are nearly Lorentzian. Since CS_2 is highly polarizable and its moment of inertia is large, the barrier height must be much greater than the rotational spacings. It therefore seems reasonable that they discuss their results as classical rotation of molecules in the liquid. The motion is therefore described in terms of molecules rotating in a homogeneous viscous medium. This classical model of rotation in the liquid state originally proposed by Debye[25] has been extended by others for interpretation of Raman results and is outlined by Shapiro and Broida.

(18) T. Fujiyama and B. Crawford, Jr., *J. Phys. Chem.*, **72**, 2174 (1968).
(19) W. G. Rothschild, *J. Chem. Phys.*, **49**, 2250 (1968).
(20) J. Shimozawa and M. Wilson, *Spectrochim. Acta*, **22**, 1609 (1966); W. G. Rothschild, *Macromolecules*, **1**, 43 (1968).
(21) H. Shimizu, *J. Chem. Phys.*, **43**, 2453 (1965).
(22) P. Datta and G. Barrow, *ibid.*, **43**, 2137 (1965); **48**, 4662 (1968); *J. Phys. Chem.*, **72**, 2259 (1968).
(23) W. West and R. Edwards, *J. Chem. Phys.*, **5**, 14 (1937); M. Bulanin and N. Orlova, *Opt. i Spektroskopiya*, **4**, 569 (1958); H. Goldring, J. Kwok, and G. Robinson, *J. Chem. Phys.*, **43**, 3220 (1965).
(24) S. L. Shapiro and H. P. Broida, *Phys. Rev.*, **154**, 129 (1967).
(25) P. Debye, "Polar Molecules," Chemical Catalogue Co., New York, N. Y., 1929.

Using the Debye model the half-width of the band shape can be used to evaluate the relaxation times for molecular reorientation. For CS_2 these times are of the order of 10^{-12} sec, which may be compared to the shorter time scale, $\sim 10^{-13}$ sec, for the lighter CH_4 molecule (see Figure 5).

Rayleigh scattering studies of larger molecules such as polyethylene glycols and alkyl bromides with variable chain lengths have been made by Pinnow, *et al.*[26] Relaxation times vary from 2×10^{-12} sec for ethyl bromide to 8×10^{-10} sec for molecules like 1-hexadecyl bromide. The larger molecules are more confined by their solvent cages and therefore take a longer time to reorient. The data are further interpreted by models which allow a distinction to be made for reorientation in terms of diffusion or jump processes depending upon the size of the molecule and its solvent cage.

For interpretations of light-scattering experiments by using time-correlation functions, papers by Pecora and Steele[27] and Gordon[16] can be consulted.

Translational Motions

The most convincing case for spectroscopic observation of translational motions in liquids comes from the studies on hydrogen. Broad absorption features which have been observed in the infrared spectrum of solid hydrogen have been assigned to combination bands (phonon branches) which involve changes in lattice energy of the crystal and internal energy of the molecules.[28] Since similar features are observed in pure liquid hydrogen and its solutions their interpretation must also include exchanges of translational energy with molecules in the liquid.

In order to consider the appearance of these translational features in a simple system let us look again at the far-infrared spectrum of a dilute solution of H_2 in liquid argon. Each of the rotational transitions shown in Figure 1 has associated with it broad absorptions which appear as shoulders. A profile analysis fits Lorentzian line shapes (not shown) to the rotational absorptions which are then subtracted from the total spectrum.[7] The resulting features indicated by a dotted curve in Figure 1 are assigned to rotation–translation transitions. As an example the feature 100 cm^{-1} to the high-frequency side of the $J = 3 \leftarrow J = 1$ transition is assigned to a rotation–translation absorption in which the rotational transition is accompanied by an increase in translational energy, $n = 1 \leftarrow n = 0$, of the H_2 trapped in its solvent cage. A weaker transition in the low-frequency side of each rotational absorption corresponds to a "hot band" in which translational deexcitation, $n = 0 \leftarrow n = 1$, accompanies the rotational transition. This translational spacing is lowered to 60 cm^{-1} when the D_2–argon solution is examined. Ewing and Trajmar[29] and Bulanin and Tonkov[30] have proposed a simple cell model to account for this type of translational absorption. The H_2 (or D_2) molecules are assumed to translate (or rattle) in their solvent cages as "localized mode" oscillators with the energy of excitation identified by the quantum number n. A simple feasibility calculation reveals that this is a reasonable assignment.[29] Consider the solute in a solvent cage as a particle in a box. The interacting molecules are assumed to be hard spheres of effective diameter $\sigma_{H_2\text{-}Ar} = 3.17$ Å. The distance between molecule centers, $a = 4.06$ Å, was calculated from $a = 2^{1/6}V^{1/3}$, where V is the molecular volume of argon determined from the density of the liquid and $2^{1/6}$ is a geometric factor assuming the arrangement of molecules in the liquid is that of the solid. Using the value $r = a - \sigma = 0.89$ Å as a radius of the cavity, the energy levels of the quantum-mechanical particle in a box may be determined. The calculated energy level difference between the first excited, $n = 1$, and ground, $n = 0$, translational states we find to be $E_1 - E_0 = 108$ cm^{-1}, in reasonable agreement with the 100-cm^{-1} spacing indicated in Figure 1. While the particle-in-a-box model is useful for feasibility calculations, a more realistic description of the translation is to consider it as an isotropic harmonic oscillator in its solvent cage.[6,29]

While these experiments give evidence for quantized translational energy levels and are in reasonable agreement with a crude cell model, it is not easy to refine the theoretical treatments to yield a detailed picture of translational motion in the liquid state. A characteristic of these induced translation transitions is that the intensity of the absorption depends on cavity size and shape. It is therefore not possible to say that the frequency associated with the maximum of absorption of a translational component necessarily corresponds to the most probable cavity configuration. A discussion of this point and a criticism of the cell model have recently been presented.[31]

The first observation of pure localized translational absorption in the liquid phase was reported by Bulanin and Tonkov.[31] They have examined H_2–Ar solutions in the region below the rotation–translation features and observed a broad absorption centered at ~ 140 cm^{-1} which is assigned to the localized translation of H_2 in its solvent cage. Another interesting feature at 38 cm^{-1} which appears also in D_2–argon solutions they tentatively assigned to phonon absorption by the liquid argon. This absorption is induced by the solute impurities (H_2 or D_2) in the liquid argon.

Further spectroscopic evidence for translational motion of molecules in liquids is available from a few other studies. Marteau, *et al.*, have examined the far-infrared collision-induced absorption of liquid

(26) D. Pinnow, S. Candau, and T. Litovitz, *J. Chem. Phys.*, **49**, 347 (1968).
(27) R. Pecora and W. Steele, *ibid.*, **42**, 1872 (1965).
(28) H. Gush, W. Hare, E. Allen, and H. Welsh, *Can. J. Phys.*, **38**, 176 (1960).
(29) G. Ewing and S. Trajmar, *J. Chem. Phys.*, **41**, 814 (1964).
(30) M. Bulanin and M. Tonkov, *Phys. Letters*, **26A**, 120 (1968).
(31) H. Welsh and R. Kreigler, *J. Chem. Phys.*, **50**, 1043 (1969); G. Ewing and H. Chen, *ibid.*, **50**, 1044 (1969).

Kr–Ar mixtures.[32] Since the solute and solvent atoms have comparable masses, it is probably appropriate to assign these absorptions to nonlocalized phonon modes of the liquid. Weak absorptions in the far-infrared of a number of simple liquids such as CS_2 or C_6H_6 have been attributed to lattice modes of the translational type;[33] however, absorption by CCl_4 has been identified with rotatory motion.[34] This absorption apparently arises from motions of dipoles induced by neighboring molecular quadrupoles or octapoles in the liquid.[35] It is difficult to distinguish induced rotational and induced translational absorption in these nonpolar polyatomic molecules since the frequencies of these motions are comparable. It would seem that further work on the liquefied rare gases will provide the most fruitful approach to the spectroscopic study of translational modes.

Rotation–Translation Coupling

In the previous discussion rotational and translational energies of molecules in liquids have been treated as unrelated. For most liquid systems, however, these motions must be considered coupled. The simplest spectroscopic example which shows the effect of this coupling is the induced rotational absorption of HD in liquid argon.[7] It has been noted that the rotational energy states of H_2 or D_2 in liquid argon are within experimental error of their gas-phase values. The rotational energy levels for HD–argon, however, are shifted in an erratic way from their unperturbed values. Friedmann and Kimel have provided a theoretical treatment which accounts for these anomalous shifts.[36] Figure 6 shows a simple cell model of an asymmetric molecule like HD trapped in a solvent cage of argon atoms. The electrical center and the center of interaction of the solute molecule (indicated by a dot) is located halfway between the two nuclei, and the center of mass (indicated by a cross) is a distance b away toward the deuterium. When the HD rotates about its center of mass the electrical center is displaced from the center of the cavity. It must then translate back into the center of the cavity to be restored to a position of minimum potential energy. Thus for HD or any molecule whose center of interaction does not coincide with the center of mass, rotational and translational motions are coupled by the solvent cavity. Assuming a spherically symmetric cavity, rigid rotor wave functions, and isotropic harmonic oscillator translational wave functions, a perturbation theory can be used to calculate shifts of the rotational levels. Besides the molecular constants for the free molecule the only parameters which are needed for the

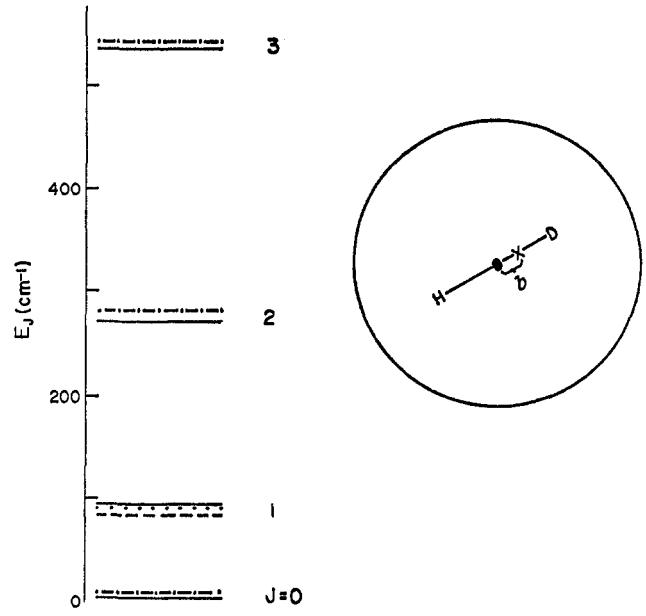

Figure 6. Translation–rotation coupling of HD in liquid argon. The energy diagram shows the rotatory levels for unperturbed HD (solid lines). The dotted lines are the theoretical HD levels after coupling of translational and rotational motions. The dashed lines indicate the experimental levels. The figure to the right represents a HD molecule trapped in an argon solvent cavity.

calculation are b and the translational energy level separation. Geometry determines $b = 0.12$ Å for HD so the translational energy separation is the only adjustable parameter. Using a value of 100 cm^{-1} which is consistent with the measured translational spacing of H_2 the perturbed rotational levels are calculated[36] and presented in Figure 6 by dotted lines. The solid lines represent the unperturbed or gas-phase HD levels[37] and the dashed lines indicate the experimental values. Qualitatively the effect of the coupling is to lend zero-point translational energy to the rotational states and raise the $J = 0, 2, 3$ levels. The $J = 1$ level is, however, lowered by a near resonance with the 100-cm^{-1} translational spacing. The agreement between theory and experiment is seen to be good. Other consequences of this coupling are evident from the spectra. The rotational band widths of HD are double those of either H_2 or D_2 solutions. The selection rules are also relaxed. Whereas only $\Delta J = +2$ transitions were observed for H_2 and D_2, $\Delta J = +1, +2, +3, +4$ transitions were detected in HD–argon. All these anomalies can be accounted for by coupling which extensively mixes translational and rotational wave functions.

The effects of translation–rotation coupling observed for HD solutions, shifts in rotational levels, broadening of rotational levels, and relaxation of selection rules, must also be present in other liquid systems. These effects, however, cannot be so easily identified in liquids other than HD because individual rotational fine structure is not resolved. Evidence that rotation–

(32) P. Marteau, R. Granier, H. Vu, and B. Voda, *Compt. Rend.*, **265B**, 685 (1967).
(33) G. Chantry, H. Gebbie, B. Lassier, and G. Wyllie, *Nature*, **214**, 163 (1967).
(34) H. Gabelnick and H. Strauss, *J. Chem. Phys.*, **46**, 396 (1967).
(35) S. Garg, J. Bertie, H. Kelp, and C. P. Smyth, *ibid.*, **49**, 2551 (1968).
(36) H. Friedmann and S. Kimel, *ibid.*, **47**, 3589 (1967).
(37) R. A. Durie and G. Herzberg, *Can. J. Phys.*, **38**, 806 (1960).

translation coupling is present in other systems is provided by the study of Kroon and Van der Elsken.[38] They have shown that the broad structureless far-infrared absorption of a polar molecule like CH_3CN in *n*-heptane is principally of rotatory origin. In more polarizable solvents like CS_2 the band intensity increases. This is accounted for by polarization which induces a larger dipole in the solvent. Since the magnitude of this induced absorption is strongly dependent on solute–solvent distances, translational motion of the molecule modulates this dipole, and it therefore contributes to the absorption.

A number of other far-infrared studies on polar and nonpolar molecules have revealed absorption features in the region 20–200 cm^{-1}.[39] Davies, *et al.*,[40] have used an interferometer to examine absorption and dispersion of small polar organic molecules in the liquid down to 2 cm^{-1}. In all of these studies essentially one broad structureless absorption is observed. Davies reviews a number of classical treatments of molecular reorientation based on Debye's early model[25] and finally considers an interpretation of the data in terms of highly hindered rotation best described as librational. The work of Kroon on similar molecules, however, would suggest that allowed rotational transitions as well as induced translational transitions contribute to the absorption. It is difficult therefore to get more than a qualitative picture of the type of rotational–translational motion that is occurring.

An advantage of Gordon's analysis discussed in a previous section is that it includes rotational–translational coupling in the definition of $\hat{\mu}(t)$ since the direction of the dipole is determined by vibration–rotation–translation in the liquid. However, the effects of induced absorption which can result from this coupling are not yet included in his discussion.

Summary

Spectroscopic evidence for quantized rotational energy levels in the liquid state is most convincing from studies of hydrogen and its isotopes where discrete rotational absorptions are observed. For small molecules such as CH_4, HCl, N_2, or O_2, infrared or Raman band shapes are broad and, although they suggest a rotational contour, no discrete rotational fine structure is observed. However, the absence of this fine structure is to be expected since the barriers to rotation are larger than the rotational spacings and the varieties of local environments and other broadening mechanisms cause these levels to blur together. A better understanding of rotational motion in liquids for these molecules can be obtained from a dipole correlation function analysis of the band shape. This yields the time dependence of the rotating molecular dipole and shows how it is hindered by intermolecular torques and interrupted by collisions in the liquid. For large molecules the band shapes do not resemble a rotational contour but are nearly Lorentzian, and classical models can be applied to understand molecular reorientation.

Spectroscopic evidence for translational motion in liquids is less clear-cut than for rotational motion. These absorptions are induced, and therefore the intensity distribution of translational bands depends upon the cavity shape and size. An analysis of translational features has only been possible, so far, for H_2–Ar where the rotational and translational motions of H_2 can be clearly separated and for mixtures of rare gases where no rotational motions are possible to obscure the analysis. Simple cell models which treat the light impurity (H_2) as a particle in a box (its solvent cavity) give qualitative understanding of the gross features. There is considerable need for theoretical analysis of this type of data. The results of such theoretical studies together with more experimental data would add to our understanding of the liquid state.

Rotation–translation coupling appears to be of considerable importance to the discussion of molecular motion in liquids when the center of interaction of a molecule differs from its center of mass. Even for a simple solution system like HD in argon rotational energy levels are shifted and rotational wave functions become mixed with translation wave functions. For more complicated systems solute–solvent polarization effects can cause translational and rotational absorption features to become indistinguishable.

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(38) S. Kroon and J. Van der Elsken, *Chem. Phys. Letters*, **1**, 285 (1967).

(39) H. Wyss, R. Werder, and H. Bunthard, *Spectrochim. Acta*, **20**, 573 (1964); E. Decamps, A. Hadni, and J. Munier, *ibid.*, **20**, 373 (1964); Y. Leray and E. Constant, *Compt. Rend.*, **264B**, 533 (1967); J. Chamberlain, E. Werner, H. Gebbie, and W. Slough, *Trans. Faraday Soc.*, **63**, 2605 (1967).

(40) M. Davies, G. Pardoe, J. Chamberlain, and H. Gebbie, *ibid.*, **64**, 847 (1968).