

Molecular-beam Spectroscopic Studies of Intermolecular Interactions

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The results of molecular-beam electric-resonance studies of weakly bound van der Waals complexes are discussed. The use of spectroscopic constants to investigate intermolecular interactions is critically examined. Potential surfaces for the interaction of rare-gas atoms and hydrogen halides are presented and their accuracy is assessed.

There have been great advances in recent years in our understanding of the interaction between two molecules. Although two molecules in close proximity each modify the mechanical and electrical properties of the other,¹ most studies have been directed towards a determination of the intermolecular forces and a description of the interaction potential surface. The combination of bulk gas properties such as second virial coefficients and the viscosity of gases with crossed molecular-beam differential scattering has led to reliable potentials for a number of atom-atom systems.² However, the situation is far more complicated for atom-molecule or molecule-molecule systems since the potential is now anisotropic in that the potential is no longer just a function of the intermolecular distance but also depends upon the relative orientation of the molecules. Most attempts to invert the data from bulk gas properties or molecular-beam scattering have led to *effective* isotropic potentials,³ since all the observed effects are some angular average over the anisotropic potential.

Information on the anisotropic interactions has been obtained by a number of spectroscopic techniques. Both pressure-broadening of rotational lines⁴ and rotational-energy transfer⁵ depend upon the anisotropic interaction during collisions. The magnitude of these effects can provide useful information on the strength of the anisotropy of the potential, but it is difficult to invert such experimental data to provide meaningful anisotropic potentials.

A more recent and a potentially far more informative approach is the detailed spectroscopy of van der Waals molecules, those weakly bound complexes held together by intermolecular forces, not covalent bonds. Since the strength of such van der Waals bonds is usually $< 5 \text{ kJ mol}^{-1}$, the dimers exist in very low concentrations at most temperatures and pressures. The equilibrium population of the complexes may be increased by lowering the temperature or raising the pressure but this is limited by the equilibrium vapour pressure of the separate components. Despite these difficulties, the infrared spectra of a number of van der Waals molecules have been observed under equilibrium conditions,⁶ but only the molecular complexes of hydrogen studied by Welsh and co-workers⁷ have been fully analysed.

MOLECULAR-BEAM SPECTROSCOPY

An efficient way of overcoming the low concentration of van der Waals molecules in equilibrium systems is to use the cold molecular beams formed by expanding a gas at high pressure through a supersonic nozzle into a vacuum. During the expansion almost the entire enthalpy of the gas is converted into directed motion of the gas. The resulting very narrow spread in the velocities of the molecules in the jet may be characterised by a very low effective translational temperature, often <1 K. Under these dynamic conditions complexes can be formed in large concentrations. The almost complete absence of collisions in such a beam also makes it an ideal environment for the study of the spectra of weakly bound complexes.

Several spectroscopic techniques have been applied to the study of complexes in a beam. Smalley *et al.* have used the technique of laser-induced fluorescence.⁸ The molecules in the beam are excited by a tunable laser and the resulting fluorescence is monitored. More recently Gough *et al.* have detected the infrared spectrum of complexes by bolometric spectrometry.⁹ Here the molecular beam is incident on a cryogenic bolometer and crossed by a tunable infrared laser. Radiation absorbed by molecules in the beam is carried to the bolometer where it is converted to heat. If photodissociation of the complex is rapid the spectrum is observed as a negative signal at the bolometer.

Despite the many recent advances in these methods, the most detailed information to date on the structure and dynamics of van der Waals molecules has been obtained in the microwave and radiofrequency region of the spectrum by molecular-beam electric-resonance spectroscopy. The supersonic nozzle beam passes through two inhomogeneous electric field regions which focus molecules in a given quantum state onto a high-sensitivity mass-spectrometer detector. Microwave or radiofrequency radiation is applied to the molecular beam between the two focusing fields and transitions are detected as a change in the beam flux at the detector.

The rotational spectra of the van der Waals molecules obtained by this method may be analysed to give spectroscopic constants similar to those for normal semi-rigid molecules. The most important are the rotational constants, the centrifugal distortion constants, the electric dipole moment and the electric quadrupole coupling constants for nuclei with $I \geq 1$. In order to use these constants to provide information on the structure and dynamics of the molecule it is necessary to assume a model for the complex. Since the van der Waals interaction is much weaker than a normal chemical bond it is normally a good approximation to assume that each of the constituent molecules retains its electrical and mechanical properties on complex formation.

The rotational constants are directly related to the inverse of the moments of inertia of the complex. If the structures of the individual molecules in the complex are known the van der Waals bond length may then be determined. This is a vibrational average of possibly large-amplitude vibrational motion associated with the weak bond, but even a simple analysis gives direct information on the equilibrium structure of the complex and hence the position of the minimum in the potential-energy surface.

The centrifugal distortion constants reflect the changes in the rotational constants due to the centrifugal forces in a rotating complex. These are related to all the bond force constants within the complex but, since the van der Waals bond is at least a factor of 100 weaker than normal chemical bonds, the observed centrifugal distortion effects are dominated by the force constants associated with the van der Waals interaction. These data provide information on the curvature of the potential around its minimum.

In pseudo-linear complexes like $\text{Ar}\cdot\text{HCl}$ there is little direct information on the

bending potential surface. It is in principle possible to observe the bending vibration of the complex by far-infrared spectroscopy, but such spectra are generally very weak and have not been observed in a beam. The only work to date was conducted in a high-pressure static cell and provides only low-resolution data.¹⁰ However, because of the large-amplitude bending motion in rare-gas-hydrogen-halide complexes, the dipole moments and quadrupole coupling constants provide information on the effective angular structure and hence on the amplitude of the bending motion. The values of the constants measured are the components of the monomer along the *a*-inertial axis. If γ is the angle between this inertial axis and the bond of the diatomic molecule, the measured dipole moment is

$$\mu_a = \mu_0 \langle P_1(\cos \gamma) \rangle + \text{small corrections}$$

where μ_0 is the dipole moment of the isolated diatomic molecule; the small corrections arising from polarisation and possible charge transfer have also been included. The polarisation correction is in principle calculable and Flygare *et al.* have provided evidence that charge-transfer effects are unimportant.¹¹ However, there is usually a large uncertainty in the polarisation correction so that the values of $\langle P_1(\cos \gamma) \rangle = \langle \cos \gamma \rangle$ also possess a large residual uncertainty.

An inherently more accurate measure of the angular geometry is provided by the quadrupole coupling constants. The measured value is again that along the *a*-inertial axis and is related to that in the free molecule *via* the second Legendre polynomial

$$\begin{aligned} eQq_a &= eQq_0 \langle (3 \cos^2 \gamma - 1)/2 \rangle \\ &= eQq_0 \langle P_2(\cos \gamma) \rangle. \end{aligned} \quad (1)$$

This is expected to be a far better approximation than that for the dipole moment. The field gradient at the nucleus is dominated by the electrons close to the nucleus and their charge distribution is almost certainly little affected by the formation of a van der Waals bond. Furthermore it is now often possible to check the consistency of this model by measuring the quadrupole coupling constant of a second nucleus within constituent molecules or by measuring the nuclear spin-spin dipolar coupling constant, d_a . Both constants should be related to the monomer constants by the same value of $\langle P_2(\cos \gamma) \rangle$. The results for Ar·HBr and Kr·HCl are summarised in table 1. All

TABLE 1.—COMPARISON OF ANGULAR EXPECTATION VALUES FOR Ar·DBr AND Kr·HCl

	$P_2(\cos \gamma)$	$\gamma_{P_2} = \arccos \langle \cos^2 \gamma \rangle^{1/2} / ^\circ$
Ar·D ⁷⁹ Br	0.520 556(10) ^a	34.4271(4)
	0.511 8(89) ^c	34.80(36)
	0.516(108) ^d	34.6(44)
Ar·D ⁸¹ Br	0.520 837(12) ^a	34.4156(5)
	0.514 0(95) ^c	34.69(39)
	0.523(104) ^d	34.3(43)
⁸⁴ Kr·H ³⁵ Cl	0.432 386(13) ^b	37.9628(5)
	0.436 5(52) ^d	37.8(2)
⁸⁴ Kr·H ³⁷ Cl	0.432 2(7) ^b	37.97(3)
	0.419 (34) ^d	38.5(13)
⁸⁴ Kr·D ³⁵ Cl	0.605 467(14) ^b	30.8543(6)
	0.604 4(46) ^c	30.9(2)
	0.51(15) ^d	35(6)

^a From $(eQq)^{\text{Br}}$; ^b from $(eQq)^{\text{Cl}}$; ^c from $(eQq)^{\text{D}}$; ^d from d_a .

26 MOLECULAR-BEAM STUDIES OF INTERMOLECULAR INTERACTIONS

the values agree within their respective experimental uncertainties; it appears that the assumptions of the model are accurate to much better than 1%.

INTERMOLECULAR POTENTIAL-ENERGY SURFACES

Although there have been few high-resolution studies of the vibrational motion of van der Waals molecules there is usually sufficient information from rotational spectra to determine an intermolecular potential-energy surface. Such spectroscopic data on van der Waals molecules have a particular advantage over those of bulk gas properties and molecular-beam scattering in that spectroscopic constants are usually of extremely high precision and are each only sensitive to one particular feature of the potential surface. In many ways, the potential surface is similar to the force field of a normal polyatomic molecule. However, because of the larger amplitude of the motions associated with the van der Waals bond, the potential can often be determined over a larger range of configuration space.

All of the currently available data are fairly insensitive to the coupling of the vibrations of the free molecule to those of the van der Waals bond; such effects have only been investigated in the hydrogen complexes.¹² The principal reason for this lack of sensitivity is the much greater frequency of normal vibrations than those associated with the van der Waals bond. The two types of motion may then be separated in a manner similar to the Born–Oppenheimer separation of electronic and nuclear motions. As a consequence the intermolecular potential that is determined is just an average over the effects of the internal motions of the constituent molecules.

In the particular case of an atom–diatom complex the Hamiltonian for the system is greatly simplified. The intermolecular potential energy is now just a function of the intermolecular distance R and the angle between R and the diatom bond. The Hamiltonian for the system can be written in the form

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + b_{\text{mol}} j^2 = \frac{\hbar^2}{2\mu R^2} (J - j)^2 + V(R, \theta) \quad (2)$$

where μ is the reduced mass of the complex, b_{mol} is the rotational constant of the diatomic molecule, j is the angular momentum of the molecule and J is the total angular momentum of the complex. The terms describe, respectively, the kinetic energy for the stretching of the van der Waals bond, the rotational energy of the molecule (which becomes a vibration in the presence of an anisotropic potential), the end-over-end rotational energy of the complex and the intermolecular potential energy.

A convenient expansion of the potential is in terms of the Legendre polynomials $P_k(\cos \theta)$ which form a complete set of angular functions. Thus

$$V(R, \theta) = \sum_k V_k(R) P_k(\cos \theta) \quad (3)$$

where $V_k(R)$ is any suitable function for a one-dimensional well, such as a Lennard–Jones function. A more realistic functional form is given by the Maitland–Smith parameterisation¹³ in which the Lennard–Jones exponent n is allowed to vary linearly with intermolecular distance. The radial potential is then written as

$$V(R) = \varepsilon \{ [6/(n-6)]x^{-n} - [n/(n-6)]x^{-6} \} \quad (4)$$

where $x = R/R_m$, R_m is the equilibrium separation, ε is the well depth and n is allowed to vary with R ,

$$n = m + \gamma(x - 1) \quad (5)$$

where m and γ are constants. The radial curvature at the minimum is independent of γ , so that γ is not determined by the rotational spectrum. γ is typically 10 for rare-gas potentials¹³ so it has been fixed at this value. In order to match the leading term in the long-range $P_1(\cos \theta)$ anisotropy, the radial potential for $k = 1$ has n replaced by 7 everywhere in eqn (4).

This leaves a large number of adjustable parameters to be determined so that the summation in eqn (3) is normally truncated at $k = 2$ or 3. Although this multipole type series converges rapidly at large intermolecular distances, there is no reason to suppose that it will do so in the region of the well. Another disadvantage of the multipole parameterisation is that the most readily determined features of the surface, such as the position of the minimum and the curvature at the minimum, are not simply related to the adjustable parameters.

An alternative, preferred parameterisation specifies the potential as a function of R at each of several values of θ . The potential at $\theta = 0, 60, 120$ and 180° is written as a Maitland-Smith function [eqn (4)] and at a given R is interpolated between these angles using the Legendre polynomials $P_0(\cos \theta)$ to $P_3(\cos \theta)$. This is referred to below as the "4-angle" parameterisation. The vibrational motion of the hydrogen halide within a complex samples the region from $\theta = 0^\circ$ to, typically, $\theta = 90^\circ$. There is little information on the potential at 120 and 180° ; these potential parameters are therefore fixed at some "physically reasonable" value.

Several methods have been applied to obtain the eigenvalues and eigenfunctions of

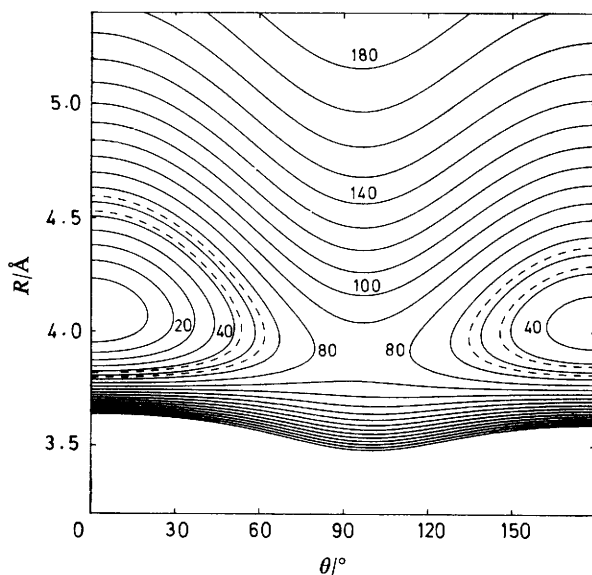


FIG. 1.—Multipole potential for Kr·HCl. Contours are at 10 cm^{-1} intervals above the minimum; the dashed curves outline the classically accessible regions for Kr·HCl and Kr·DCl.

eqn (2). The close coupling¹⁴ and the secular equation¹² methods have been favoured by some, but the most efficient appears to be the angular-radial separation method of Holmgren *et al.*¹⁵ The eigenfunctions are assumed to be the simple product $\phi(\theta; R)\chi(R)$ of an angular and a radial function. Initially the angular problem is solved at each value of R using free-rotor spherical harmonics as basis functions. This yields eigenfunctions $\phi_b(\theta; R)$ and eigenvalues $U_b(R)$ which depend parametrically on R .

28 MOLECULAR-BEAM STUDIES OF INTERMOLECULAR INTERACTIONS

$U_b(R)$ provides an effective potential for the radial motion from which $\chi(R)$ may be determined.

This procedure is a fairly good approximation providing $\phi_b(\theta; R)$ is a slowly varying function of R . For accurate calculations, however, the neglected non-adiabatic coupling of different $\phi_b(\theta; R)$ must be included: a rapid procedure developed by Hutson has been used.¹⁶

A least-squares fit to the rotational spectra of the different isotopic forms of a number of atom-diatom complexes has been performed using both the multipole and "4-angle" parameterisations. Fig. 1 and 2 show the results for Kr·HCl. The data

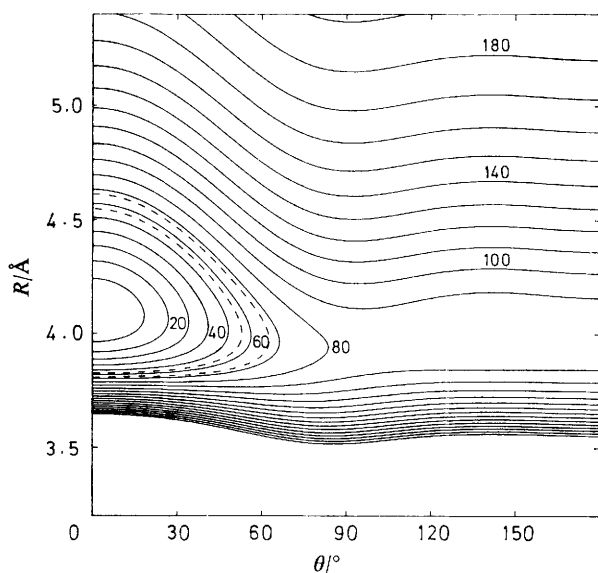


FIG. 2.—"4-angle" potential for Kr·HCl. Contours are at 10 cm^{-1} intervals above the minimum; the dashed curves outline the classically accessible regions for Kr·HCl and Kr·DCl.

are insensitive to the absolute well depth, so that the isotropic well depth was set at 155 cm^{-1} by scaling the molecular-beam scattering results of Farrar and Lee for Ar·HCl.³ The multipole potential expansion was truncated at $P_2(\cos \theta)$. The repulsive wall parameters m for the anisotropic potential were constrained to the same value as the isotropic m ; the values of R_m in $V_1(R)$ and $V_2(R)$ were constrained to be the same, but different from the value in $V_0(R)$. This gives a potential with just 5 adjustable parameters. The "4-angle" potential was also constrained to 5 parameters. The $\theta = 0$ and 60° well depths were allowed to float, while those at $\theta = 120$ and 180° were fixed at the same value to one another. The wall parameter m was constrained to be the same at all angles. Lastly, R_m was allowed to take different values at $\theta = 0$ and 60° but the values of R_m at 120 and 180° were forced to be the same as that at 60° .

A comparison of the two potentials is physically illuminating. The multipole potential possesses a large secondary minimum at $\theta = 180^\circ$ whereas this is precluded in the "4-angle" potential. However, within the classically accessible region around $\theta = 0^\circ$ the two potentials have a very similar shape. Thus although the results should be reliable in this classically accessible region, potentials obtained from spectroscopic data should not be extrapolated far beyond the classical turning points.

CONCLUSION

Spectroscopic data can be used to determine the shape of the well in the region of the potential minimum. However, in order to determine the entire potential surface it is essential to include the data from many different experiments. We are currently combining the results of molecular-beam scattering, rotational line-broadening and second virial coefficients with spectroscopic data of the van der Waals complex to determine the potential for $\text{Ar}\cdot\text{HCl}$.¹⁷

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¹ H. L. Welsh, *M.T.P. International Review of Science, Physical Chemistry, Series One*, 1972, **3**, 33; J. Van Kranendonk, *Physica*, 1958, **24**, 347.

² For example H. J. Hanley, J. A. Barker, J. M. Parson, Y. T. Lee and M. Klein, *Mol. Phys.*, 1972, **24**, 11.

³ J. M. Farrar and Y. T. Lee, *Chem. Phys. Lett.*, 1974, **26**, 428; U. Buck and P. McGuire, *Chem. Phys.*, 1976, **16**, 101.

⁴ J. G. Kircz, G. J. Q. van der Peyl, J. van der Elsken and D. Frenkel, *J. Chem. Phys.*, 1978, **69**, 4606.

⁵ T. Oka, *Adv. Atom. Mol. Phys.*, 1973, **9**, 127.

⁶ For example M. Laver, J.-P. Houdeau and C. Haesler, *Can. J. Phys.*, 1978, **56**, 334; C. A. Long and G. E. Ewing, *J. Chem. Phys.*, 1973, **58**, 4824.

⁷ A. R. W. McKellar and H. L. Welsh, *J. Chem. Phys.*, 1971, **55**, 595; *Can. J. Phys.*, 1972, **50**, 1458; 1974, **52**, 1082.

⁸ D. H. Levy, *Adv. Chem. Phys.*, 1981, to be published.

⁹ T. E. Gough, R. E. Miller and G. Scoles, *J. Chem. Phys.*, 1978, **68**, 1588.

¹⁰ E. W. Boom and J. van der Elsken, *J. Chem. Phys.*, 1980, **73**, 15.

¹¹ M. R. Keenan, L. W. Buxton, E. J. Campbell, T. J. Balle and W. H. Flygare, *J. Chem. Phys.*, 1980, **73**, 3523.

¹² R. J. LeRoy and J. Van Kranendonk, *J. Chem. Phys.*, 1974, **61**, 4570.

¹³ G. C. Maitland and E. B. Smith, *Chem. Phys. Lett.*, 1973, **22**, 443.

¹⁴ A. M. Dunker and R. G. Gordon, *J. Chem. Phys.*, 1976, **64**, 354.

¹⁵ S. L. Holmgren, M. Waldman and W. Klemperer, *J. Chem. Phys.*, 1977, **67**, 4414; *J. Chem. Phys.*, **69**, 1661.

¹⁶ J. M. Hutson and B. J. Howard, *Mol. Phys.*, 1980, **41**, 1123.

¹⁷ J. M. Hutson and B. J. Howard, *Mol. Phys.*, 1981, to be published.