

is in agreement with the formation of a carbonium ion rather than with a concerted 1,2 shift.⁵⁷

Conclusions

The above discussion emphasizes that the application of the appropriate acidity function, and hence a knowledge of the acid-base behavior of substrates, is *conditio sine qua non* to deduce mechanistic implications even from otherwise accurate kinetic analysis of acid-catalyzed reactions. As shown by the case of substituent effects on the reduction by iodide ions of sulfoxides, the observed rate changes as a function of structural factors often result from a combination of effects on basicity and on reaction rates.

On the other hand, it is clear that there is no meaning in an "absolute" measure of the strength of a base or an acid,¹⁵ since solvation phenomena have a very large effect in determining the ionization ratios of each class of base (or each base) in every solvent. As an example we recently observed^{58,59} that solvation requirements of dialkyl ethers (ϕ ca. +0.8)⁵⁹ and sulfides (ϕ ca. -0.2)⁵⁸ are very different. They make the log *I* values of sulfides larger than those of ethers in the stronger acid solutions (H₂SO₄

(57) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold Co., New York, N. Y., 1970.

(58) P. Bonvicini, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 2267 (1972).

(59) P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, manuscript in preparation.

> 65%). These results match well with the recent findings that, whereas dialkyl ethers are more basic than sulfides in dilute acids by ca. 4 pK_{BH+} units,⁵⁹ the reverse is true in the gas phase where the proton affinity of H₂S is ca. 14 kcal/mol higher than that of H₂O.⁶⁰

It is precisely the comparison between the liquid and gas phase, made possible by recent improvements in experimental techniques,⁶¹ which could well lead to the most important progress in the field of acid-base equilibria, hopefully making possible a dissection of the thermodynamic quantities (ΔH° , ΔG° , ΔS°) into ionization and solvation terms.⁶² This will lead to a greater understanding of solvent effects in organic chemistry, which is the ultimate purpose of most acid-base equilibrium investigations.¹⁵

Most of the work here described has been made possible through a close collaboration with Professors D. Landini, G. Modena, and F. Montanari, to whom I am greatly indebted. The collaboration of other people of this research group, whose names are cited in the references, and the financial support of the Consiglio Nazionale delle Ricerche are also gratefully acknowledged.

(60) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

(61) J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, **4**, 114 (1971); J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971); P. Kebarle in "Ions and Ion Pairs in Organic Reactions," M. Szwarc, Ed., Vol. 1, Wiley-Interscience, New York, N. Y., 1972.

(62) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

Long-Lived States in Atom-Molecule Collisions

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Encounters involving an isolated pair of atoms or molecules may be characterized by collision times, τ_c . The collision time is the delay suffered by these particles with respect to their free-passage time through the collision region, as a result of their interaction.

A collision time depends on the relative velocity, v , of the pair, on the impact parameter, b , and on the intermolecular forces at play. For most values of v and b , reactants transform into products by a di-

rect process and τ_c is a smooth function of these variables, approximately equal to the period of rotation of the pair of $\tau_{dir} \approx 2\pi b/v$.

However, in the neighborhood of certain velocities v_r and impact parameters b_r a resonance process may take place, at which τ_c shows a sharp peak and increases over its previous value by a quantity $\tau_{res} \gg \tau_{dir}$ at the maximum. This second process corresponds physically to formation of a temporarily bound complex whose nature depends on whether the collision partners contain open or closed shells, and on quantities such as ionization potentials and electron affinities. The pair may temporarily form a chemical bond, a charge-transfer complex, or a van der Waals complex, in the last case as a result of the attraction of fluctuating charge distributions. Examples of these different types are provided by K + RbCl, K + SO₂ and Ar + H₂.

David A. Micha was born in Argentina, where he did his undergraduate studies at the University of Cuyo, Bariloche. He received the Filosofie Licenciati (1965) and Filosofie Doctor (1966) degrees at Uppsala University. He then worked at the Theoretical Chemistry Institute of the University of Wisconsin (Madison) and at the Institute for Pure and Applied Physical Sciences of the University of California, La Jolla. He became a Docent of Uppsala University in 1968, was Visiting Lamberg Professor at the University of Gothenburg in 1970, and is now Associate Professor at the University of Florida. He is interested in molecular electronic structure and dynamics and related computational methods.

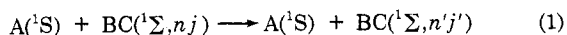
The dynamics of these collisions may be extracted from time-independent scattering states which show that resonances correspond to quasi-bound states with energies E_r and widths Γ_r . In a time-dependent description these last states have a lifetime $\tau_{\text{res}} = \hbar/\Gamma_r$. Many features of their behavior are independent of the nature of the complex and may be dealt with simultaneously. We shall refer to these states, when $\tau_{\text{res}} \gg \tau_{\text{dir}}$, as long-lived states (LLS).

The *a priori* calculation of LLS requires information on the intermolecular forces and solution of the collisional energy transfer or rearrangement problem. Intermolecular forces are best known for van der Waals complexes, and a dynamical description may be more thoroughly done for these. A few years ago we undertook an investigation of lifetimes of van der Waals complexes (specifically in collisions of noble gas atoms with hydrogen and deuterium molecules) to establish whether they would be detectable in molecular beam experiments and, if so, what information they would provide on intermolecular forces.^{1,2} In the meantime, several interesting developments have occurred: (a) long-lived van der Waals complexes have been detected by means of collision-induced infrared spectra, in the same systems we had considered; (b) molecular beam experiments indicate the presence of LLS in a number of nonreactive and reactive systems (other than van der Waals complexes), to which the same concepts may be applied; and (c) new statistical models and computational approaches, that promise to bring a deeper understanding of the subject, have been developed. We present here some of our earlier conclusions and discuss their relation to the mentioned developments.

In what follows, we describe atom-molecule potentials and spectra and the means by which LLS have been detected, we outline the collision dynamics of these states, and we comment on a number of investigated systems. We discuss in some detail the role of angular momentum coupling and of anisotropy of the potentials and the resulting angular distributions. The notation is for the most part that used in ref 2. Other recent accounts have considered some aspects of ion-molecule and molecule-molecule collisions.³

Atom-Diatomic Interactions and Spectra

The mechanism leading to van der Waals LLS is most simply discussed for a 1S atom colliding with a $^1\Sigma$ diatomic molecule (eq 1, where n and j are vibration and rotation quantum numbers). The interac-



tion potential V is then only a function of the diatom distance r , the intermolecular distance R , and the orientation angle γ between \mathbf{R} and \mathbf{r} (see Figure 1). Both the short-range (repulsive) and the long-range

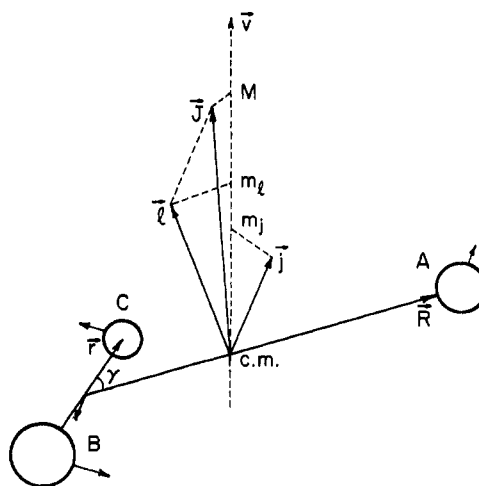


Figure 1. Relative position vectors \mathbf{R} and \mathbf{r} for the collision of atom A and diatom BC. The z axis has been chosen along the initial relative velocity \mathbf{v} . The angular momenta \mathbf{j} , \mathbf{l} , and \mathbf{J} in units of \hbar and their projections m_j , m_l and M are also shown.

(attractive) interactions are anisotropic and may be expanded in Legendre polynomials $P_l(\cos \gamma)$, with coefficients that depend on R and r . For a homonuclear diatomic we have

$$V(R, r, \gamma) = V'(R, r)[1 + b_2' P_2(\cos \gamma)] + V''(R, r)[1 + b_2'' P_2(\cos \gamma)] \quad (2)$$

with V' and V'' the isotropic short- and long-range terms. The sum $V' + V''$ may be described at the diatomic equilibrium distance r_e by, e.g., a Lennard-Jones (12,6) potential (eq 3), with ϵ and R_m the well

$$v(R) = \epsilon[(R_m/R)^{12} - 2(R_m/R)^6] \quad (3)$$

depth and its position. Terms with odd-order Legendre polynomials would also appear in V for heteronuclear diatomics. The long-range anisotropy coefficients may be accurately determined from our knowledge of electrostatic, induction, and dispersion forces. On the other hand, the short-range coefficients are unknown except in a few cases (such as $\text{He} + \text{H}_2$), and it is of interest to find processes which would provide information about their magnitude.

The relative motion of an atom-molecule pair is governed by an effective potential V_L which equals the sum of V and the centrifugal potential for orbital angular momentum \mathbf{l} . The anisotropy of V_L leads to coupling of the diatomic rotational angular momentum \mathbf{j} with \mathbf{l} , as illustrated in Figure 1, to give a total $\mathbf{J} = \mathbf{l} + \mathbf{j}$ which is a constant of motion. The probability of a given coupling may be expressed in terms of the vibration-rotation wave function $u_{n, j m_j}(\mathbf{r})$ of the diatom and the wave function $Y_l^{m_l}(\Omega)$ for rotation of the intermolecular axis. These combine to give states

$$y_{J l j n}^M(\Omega, \mathbf{r}) = \sum_{m_l m_j} \langle l j m_l m_j | J M \rangle i^l Y_l^{m_l}(\Omega) u_{n, j m_j}(\mathbf{r}) \quad (4)$$

where the $\langle l j m_l m_j | J M \rangle$ are readily available angular momentum coupling coefficients.¹³ Using these new

(1) D. A. Micha, *Chem. Phys. Lett.*, **1**, 139 (1967).

(2) D. A. Micha, *Phys. Rev.*, **162**, 88 (1967); erratum: the equations and values for Γ in ref 1 and 2 must be multiplied by N_c of p 94 of this reference.

(3) Some of these are covered in (a) R. Wolfgang, *Accounts Chem. Res.*, **2**, 248 (1969); **3**, 48 (1970); (b) B. H. Mahan, *ibid.*, **1**, 217 (1968); **3**, 393 (1970); (c) R. D. Levine, *ibid.*, **3**, 273 (1970); (d) R. Bersohn, *Comments At. Mol. Phys.*, **1**, 84 (1969).

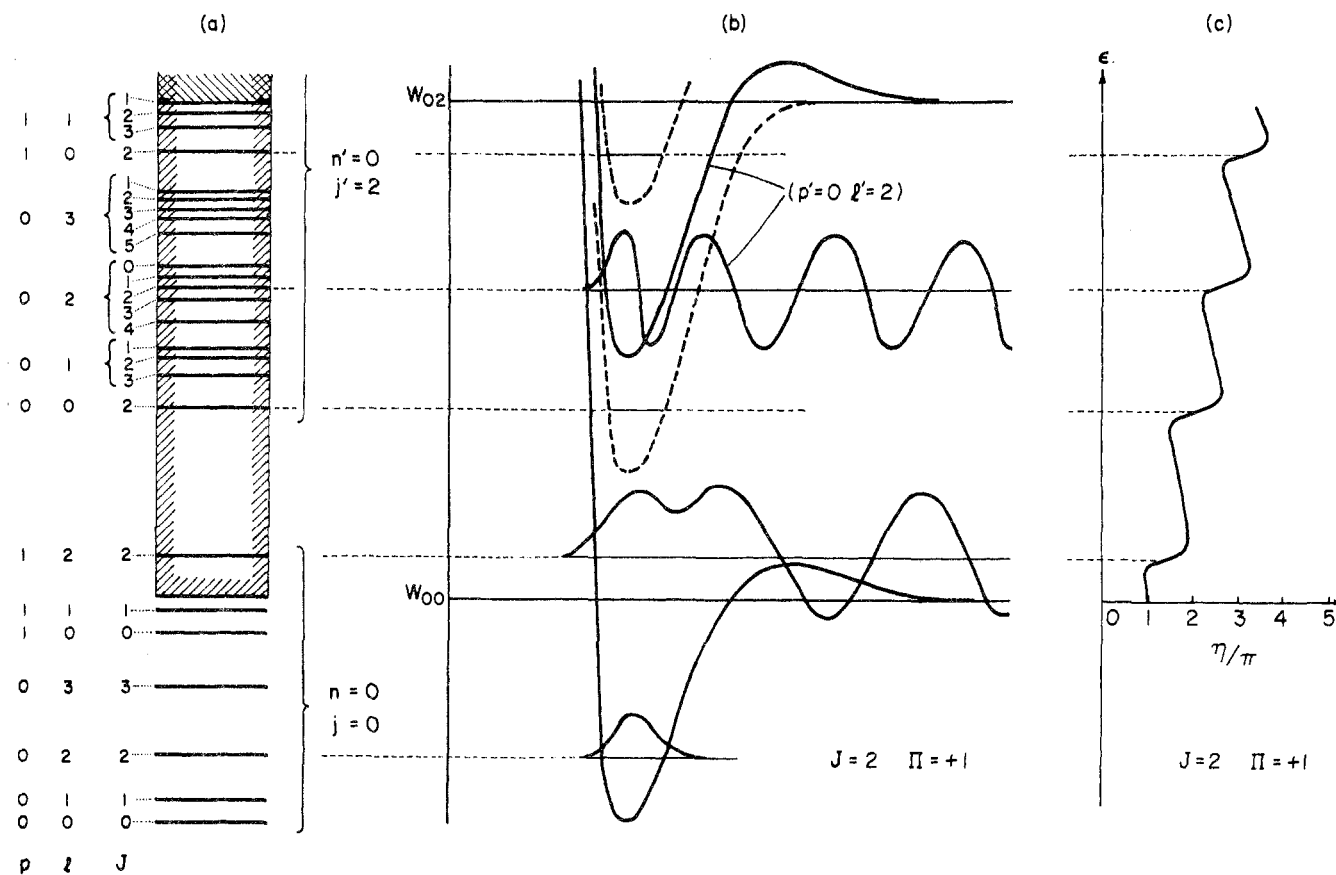
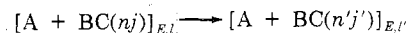


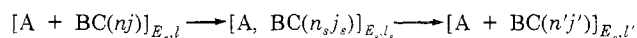
Figure 2. (a) Spectrum of an atom-homonuclear diatomic van der Waals complex; n and j are the diatomic vibration and rotation quantum numbers and W_{nj} its energy; p , l and J are the quantum numbers for vibration of the complex, orbital, and total angular momenta. (b) From bottom to top, potentials and wave functions for the bound state, orbiting resonance, and a compound-state resonance with $J = 2$, parity $\Pi = +1$. (c) Corresponding scattering phase shift as a function of the collision energy ϵ . This figure is schematic.

states the potential V_L is given by a matrix, and it is found that the quantum numbers J , M , and the total parity Π ($=(-1)^{l+j}$) are conserved during the interaction and that the energy spectrum of the atom-molecule pair may be classified according to values of J and Π , but is independent of M .

To describe the spectrum we choose the total energy E equal to zero for the atom and diatom in their ground state ($n = 0$, $j = 0$), far removed from each other and with no relative kinetic energy. We can then distinguish two regions. (a) At negative energies bound van der Waals states exist, which may be labeled by a new quantum number p besides J and Π . Their "parent" state is $n = 0$, $j = 0$; hence $J = l$, $\Pi = (-1)^J$, and the eigenenergies are simply designated E_p^J . (b) At positive energies we find a continuum of eigenenergies corresponding to scattering states. This continuum has a smoothly varying density of states from the direct collisions



and superposed on this a spectrum of long-lived states with resonance energies E_s and level widths Γ_s for which the spectral density is high. These LLS arise in the collision events



and their origin is twofold. In some instances they are *orbiting resonances* (or shape resonances) where

the pair is held together for some time by the centrifugal barrier. This may occur before any energy is transferred, leading to an *entrance channel* resonance, or after energy is transferred, which leads to an *exit channel* resonance. In some other instances the pair transfers its relative kinetic energy to internal motion of BC and for some time forms a quasi-bound state (A,BC \dagger) with total internal energy below that of separated A and excited BC \dagger , and we have a *compound-state resonance* (or Feshbach resonance). The energies of any of these LLS may be designated by $E_{njl,p}^J$.

The above features are illustrated in Figure 2a, drawn for an atom-molecule pair, for only the low-energy region of the spectrum and for the lowest $p = 0, 1$ levels. Multiplets appear for the diatomic parent state $n = 0$, $j = 2$ as a result of angular momentum coupling. For weak coupling, resonances are determined mostly by l and multiplets from $|l - 2| < J < l + 2$ lie close by, so that we may indicate these levels by $(njl,p)_J$. For strong coupling it is J that determines the positions of the levels, and multiplets arise from $|J - 2| < l < J + 2$, which we may designate by $(njJ,p)_l$. Figure 2a shows a weak-coupling case, where the low-lying resonances are orbiting ones.

Figure 2b gives diagonal matrix elements of V_L for the (A,BC) pair with $J = 2$, $\Pi = +1$. Their shape depends on $l = J, J \pm 2$, for (A,BC \dagger). Wave functions correspond to a bound state, an orbiting resonance, and a compound-state resonance. In this case only

Table I
Resonance Energies E_r and Widths Γ_r for the Low-Lying Compound States of Xe Quasi-Bound to para- H_2 , Divided by the Well Depth $\epsilon = 1.2 \times 10^{-14}$ Erg

| l | J | E_r/ϵ | | $(\Gamma_r/\epsilon) \times 10^3$ | |
|-----|-----|----------------|----------------|-----------------------------------|----------------|
| | | A ^a | B ^b | A ^a | B ^b |
| 0 | 2 | 5.55 | 5.45 | 4.50 | 4.87 |
| 1 | 3 | | 5.48 | | 5.11 |
| | 1 | 5.56 | 5.55 | 0.91 | 1.50 |
| 2 | 4 | | 5.53 | | 4.93 |
| | 2 | 5.60 | 5.57 | 1.79 | 1.62 |
| | 0 | | 5.59 | | 1.86 |
| 3 | 5 | | 5.58 | | 4.57 |
| | 3 | 5.66 | 5.61 | 2.08 | 1.62 |
| | 1 | | 5.64 | | 1.44 |

^a From ref 2. ^b From ref 4b.

elastic scattering occurs, and we have three *sub-threshold* compound-state resonances, those with $\Pi = +1$, and one orbiting resonance. This figure makes clear the connection between both types of resonances. Looking, *e.g.*, to the $p' = 0$, $l' = 2$, $J = 2$ compound-state resonance we see that as J increases the potential rises, the resonance energy moves above W_{02} (the BC⁺ internal energy), and the mechanism becomes that of an orbiting resonance.

Table I gives the lowest-lying resonance energies and widths for para-hydrogen-xenon. Columns A list the results first obtained by us to lowest order in the anisotropies and in $(R_m k)^{-1}$, with k the collision wave number, and using the potential parameters $R_m = 3.9 \times 10^{-8}$ cm, $\epsilon = 1.2 \times 10^{-14}$ erg, $b'' = 0.09$ ($\pm 10\%$), and $b' = 0.5$ ($\pm 30\%$). Within these approximations there is no multiplet splitting, so that $l = J$ and E_s , Γ_s are the same for each multiplet. More accurate results obtained recently by Muckerman and Bernstein with the same potential parameters are shown in columns B.⁴ Orders of magnitude are seen to remain unchanged. The levels follow weak-coupling ordering with the exceptions of $(njl, p)_J = (022, 0)_4$ and $(023, 0)_5$. Lifetimes obtained from $\tau_s = \hbar/\Gamma_s$ are between 10^{-10} and 10^{-11} sec.

Long-lived states with these lifetimes could in principle be detected in crossed molecular beam experiments, by searching for resonance structures in cross sections. However, these structures are highly localized in energy, for isolated LLS, and very well-defined beam energies are needed to detect them.

Infrared Absorption Spectra Induced by Collisions

Another likely form of detecting LLS is to observe the absorption spectra of collision pairs in the gas phase. In this way, isolated LLS have now been observed in a beautiful set of experiments by Welsh and collaborators⁵ published during the last year, on the infrared spectra of mixtures of noble gas atoms with hydrogen and deuterium molecules. Transitions involving bound van der Waals states have been re-

corded and studied⁶ for some time, but by conducting new experiments at lower densities (1 to 2 amagat) and at low temperatures (85 to 158°K) a fine structure has been found in the spectra which involves the multiplets of LLS of the complexes. Their lifetimes are limited by collisions, suggesting that τ is of the order of the time between collisions.

In brief description, during a collision the molecule and atom form a temporary dipole, which absorbs radiation. The dipole arises at large distances from coupling of the molecular quadrupole to an induced atomic dipole and at small distances from distortion of the electron distributions. The selection rules for collision-induced transitions⁷ are the usual dipolar ones for the overall system, $\Delta J = 0, \pm 1$ and $\Delta \Pi = -1$, plus the ones from induction $\Delta l = l_f - l_i = -3, -1, +1, +3$ corresponding to N, P, R, and T rotational branches respectively. These transitions have been observed accompanying the diatomic branches $Q_1(0)$, $S_1(0)$, $Q_1(1)$ and $S_1(1)$, *i.e.*, $n = 0 \rightarrow 1$ and $j = 0 \rightarrow 0, 2$ or $j = 1 \rightarrow 1, 3$, transitions for H_2 and D_2 . The spectra, analyzed so far using the terms

$$T_{A-H_2}(njl, p) = T_{H_2}(nj) + G(p) + B_p l(l+1) - D_p l^2(l+1)^2 \quad (5)$$

where H_2' is the perturbed H_2 molecule, indicated a weak coupling situation. The multiplicities of the atom-diatom rotational branches for each band of the diatom may be readily obtained. We show in Figure 3a some of the transitions that apply to the $S_1(1)$ branch of H_2 and the $T(l)$ branch of $A-H_2$, which has multiplicities 3, 6, and 6 for $l = 0, 1$, and ≥ 2 , respectively. A multiplet structure is very clear in this branch of the measured spectra^{5b} for Ar, Kr, and Xe + H_2 (Figure 3b).

All these spectra contain information on short-range anisotropies, which are little known and which could be obtained from a theoretical analysis of the relevant dynamics.^{6c}

Collision Dynamics of Long-Lived States

It is convenient to classify the scattering channels, defined by the asymptotic internal states of the pair and by the collision energies, into *open channels* if they are energetically accessible and *closed channels* if they are not. Consider for simplicity only one open (elastic) channel o and one closed (resonance) channel c. We omit the angular momentum indices and assume weak angular momentum coupling.

For vanishing anisotropies the channels are uncoupled and the elastic scattering state χ satisfies eq 6-8,

$$\left[\frac{d^2}{dR^2} + k^2 - U_{oo}(R) \right] \chi_o(R) = 0 \quad (6)$$

$$\chi_o(R) \sim -k^{-1/2} \{ \exp[-i(kR - l\pi/2)] - \exp[i(kR - l\pi/2)] S_{oo}^d \} \quad (7)$$

$$S_{oo}^d = \exp(2i\eta_d) \quad (8)$$

(4) (a) J. T. Muckerman and R. B. Bernstein, *J. Chem. Phys.*, **52**, 606 (1970); (b) *Chem. Phys. Lett.*, **4**, 183 (1969).

(5) (a) A. K. Kudian and H. L. Welsh, *Can. J. Phys.*, **49**, 230 (1971); (b) A. R. W. McKellar and H. L. Welsh, *J. Chem. Phys.*, **55**, 595 (1971).

(6) (a) R. G. Gordon and J. K. Cashion, *J. Chem. Phys.*, **44**, 1190 (1966); (b) J. K. Cashion, *ibid.*, **45**, 1656 (1966); (c) work is in progress by Dunker and Gordon (private communication).

(7) (a) J. Van Kranendonk, *Physica*, **23**, 825 (1957); **24**, 347 (1958); (b) J. Van Kranendonk and Z. J. Kiss, *Can. J. Phys.*, **37**, 1187 (1959).

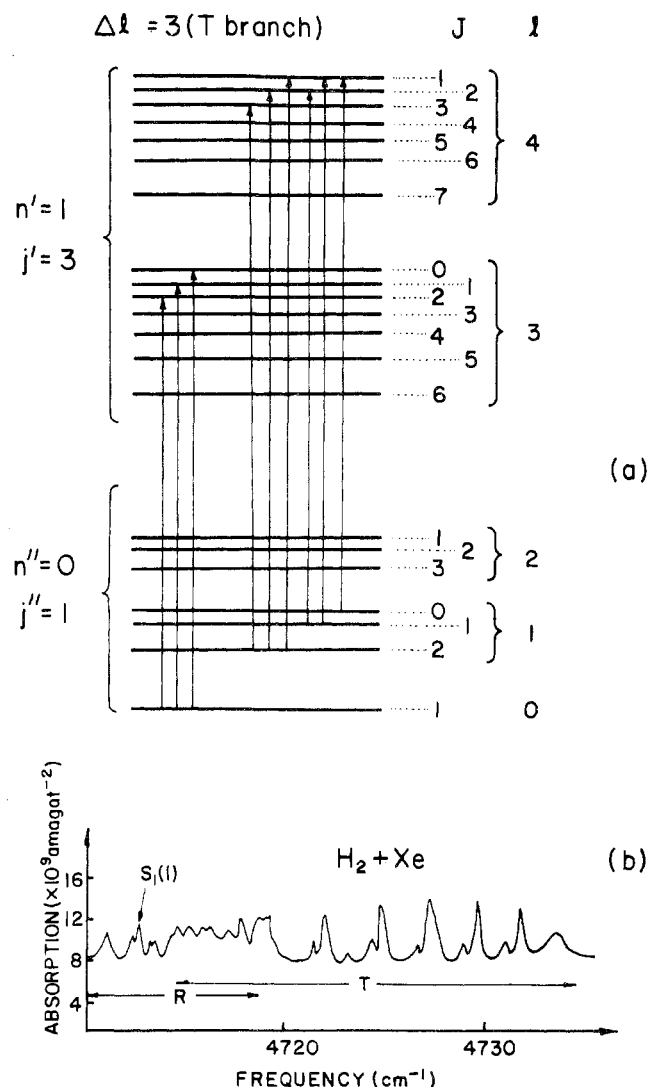


Figure 3. (a) A portion of the collision-induced absorption spectrum for an atom-homonuclear diatomic complex. Diagram is for the $S_1(1)$ branch of the diatomic ($n' = 1$, $\Delta n = 1$, $\Delta j = 2$) and the accompanying T branch of the complex ($\Delta l = 3$). (b) A portion of the same spectrum, measured by McKellar and Welsh.^{5b} The doublet structure has been ascribed to the existence of resonance multiplets.

where U_{00} is a potential such as the lowest one in Figure 2b in units of $\hbar^2/(2\mu)$, with μ the reduced mass, S_{00}^d is the scattering probability amplitude (an element of the S matrix) and η_d is the phase shift for direct scattering. This last is equal at $k = 0$ to $\pi \times$ (number of bound states) of given J and varies smoothly with energy except at orbiting resonances, such as the one shown for $J = 2$ in Figure 2c. The $s = r$ resonance state becomes, in the limit of zero anisotropies, a bound state satisfying eq 9, for

$$\left[\frac{d^2}{dR^2} + (\kappa_r')^2 - U_{cc}(R) \right] z_r'(R) = 0 \quad (9)$$

the energy $\mathcal{E}_r' = \hbar^2(\kappa_r')^2/(2\mu)$, with U_{cc} corresponding to one of the higher potentials in Figure 2b. As the anisotropy is introduced the potentials U_{00} and U_{cc} are modified and a coupling, U_{oc} , arises. The state z_r' changes into a quasi-bound (or compound) state $z_r(R)$ with complex energy

$$\mathcal{E}_r = \mathcal{E}_r' + \Delta_r - i\Gamma_r/2 = E_r - i\Gamma_r/2 \quad (10)$$

where Δ_r and Γ_r are the resonance shift and width, and χ_0 changes into a ψ_0 whose asymptotic form gives a new $S_{00} = \exp(2i\eta)$ with

$$\eta = \eta_d + \eta_r = \eta_d + \tan^{-1}[\frac{1}{2}\Gamma_r/(E - E_r)] \quad (11)$$

The last term in η introduces jumps of π at each compound state resonance energy, which add to the background phase shift as shown in Figure 2c. To lowest order in the anisotropy one has explicitly $E_r = \mathcal{E}_r'$ and

$$\Gamma_r = \frac{\hbar^2}{4\mu} |\langle z_r' | U_{oc} | \chi_0 \rangle|^2 \quad (12)$$

These are the equations used to calculate columns A of Table I. More accurate results may be obtained using adiabatic potentials as proposed by Levine.⁸ An extension of his approximation, taking due account of angular momentum coupling, was employed to obtain columns B. The most accurate calculations have been performed within the coupled-channel method,^{9,10} which gives the exact answer for a fixed number of open and closed channels. Since z_r' decreases exponentially as R grows, eq 12 shows that level widths are sensitive to the short-range features of the interaction.

When considering several open and closed channels and angular momentum coupling, we get for each J, l a matrix, S_{00} , with rows and columns labeled by $\lambda = (nj'l)$, and several resonances $s = (\lambda, p)$. The S matrix is given by eq 13, where the c_{os} are

$$S_{00} = S_{00}^d - i \sum_s (S_{00}^d)^{1/2} \frac{\Gamma_s}{|E - E_s + i\Gamma_s/2|} c_{os}^* (S_{00}^d)^{1/2} \quad (13)$$

column matrices related to transitions from the compound state s to the open-channel states.¹¹ Using this matrix the differential cross section for $(nj) \rightarrow (n'j')$ may be written in the form of eq 14, where the

$$d\sigma_{n'j'nj}^*/d\Omega = k_{n'j'}^{-2} (2j+1)^{-1} \sum_L B_L(n'j', nj) P_L(\cos \Theta) \quad (14)$$

B_L contain, besides S_{00} , angular momentum coupling coefficients.

Applications to Atom-Molecule Systems

The concepts previously discussed may be applied to a number of chemical systems in which recent beam experiments indicate formation of compound states. In most cases we expect a large number of isolated (as opposed to interfering) resonances coupled to many open channels lying within the range

(8) (a) R. D. Levine, *J. Chem. Phys.*, **49**, 51 (1968); (b) R. D. Levine, B. R. Johnson, J. T. Muckerman, and R. B. Bernstein, *ibid.*, **49**, 56 (1968).

(9) (a) W. Erlwein, M. Von Seggern, and J. P. Toennies, *Z. Phys.*, **211**, 35 (1968); (b) M. Von Seggern and J. P. Toennies, *ibid.*, **218**, 341 (1969).

(10) P. G. Burke, D. Scrutton, J. H. Tait, and A. J. Taylor, *Proc. Phys. Soc., London (At. Mol. Phys.)*, **2**, 1155 (1969).

(11) The general treatment may be found in (a) H. Feshbach, *Ann. Phys. (New York)*, **19**, 287 (1962), and in ref 2.; see also (b) B. C. Eu and J. Ross, *J. Chem. Phys.*, **44**, 2467 (1966); (c) T. F. George and J. Ross, *ibid.*, **56**, 5786 (1972).

Table II
Some of the Atom-Molecule Pairs Where Formation of Long-Lived States Appears Established

| System | Ref | Method of observation |
|--|------|--|
| Nonreactive Events | | |
| (1) o-and p-H ₂ + A o-and p-D ₂ + A A = Ar, Kr, Xe | a, b | Computational; collision-induced infrared absorption |
| (2) He + H ₂ | c | Computational |
| (3) He + N ₂ | d | Computational |
| (4) Ne + N ₂ | e | Computational |
| (5) Ar + TIF | f | Computational |
| (6) M + SO ₂ , CO ₂ M = K, Cs | g, h | Angular distribution from crossed beams; computational |
| Reactive Events | | |
| (1) M + XM' → MX + M' M, M' = alkali, TI X = halide | i, j | Angular distributions; computational |
| (2) Cl + IBr → ClI + Br | k | Angular distributions |
| (3) H + Cl ₂ → HCl + Cl | l | Computational |
| (4) Li + SnCl ₄ → LiCl + SnCl ₃ | } m | Angular distributions |
| (5) Li + PCl ₃ → LiCl + PCl ₂ | | |
| (6) Li + SF ₆ → LiF + SF ₅ | } n | Population of product internal states |
| (7) Cs + SF ₆ → CsF + SF ₅ | | |
| (8) Cs + SF ₄ → CsF + SF ₃ | } o | Angular distributions |
| (9) F + C ₂ H ₄ (C ₂ D ₄) → C ₂ H ₃ F (C ₂ D ₃ F) + H (D) | | |
| (10) Ba + O ₂ → BaO + O | p, q | Induced fluorescence; angular distributions |

^a References 2, 4, 18. ^b Reference 5. ^c References 8b, 4a, 18. ^d References 9b, 4a. ^e Reference 10. ^f J. Van de Ree, *J. Chem. Phys.*, **54**, 3249 (1971). ^g D. O. Ham and J. Kinsey, *J. Chem. Phys.*, **48**, 939 (1968); **53**, 285 (1970); D. Beck and H. Förster, *Z. Phys.*, **240**, 136 (1970). ^h A. Bjerre, "Proceedings of the VIIth International Conference on Physical, Electronic, and Atomic Collisions," North Holland, Amsterdam, 1971, p 7. ⁱ W. B. Miller, S. A. Safron, and D. R. Herschbach, *Discuss. Faraday Soc.*, **44**, 108 (1967); G. A. Fisk, J. D. McDonald, and D. R. Herschbach, *ibid.*, **44**, 228 (1967); D. Herschbach, "Proceedings of the Conference on Potential Energy Surfaces in Chemistry" W. A. Lester Jr., Ed., IBM Labs., San Jose, Calif., 1971; G. H. Kwei, A. B. Lees, and J. A. Silver, *J. Chem. Phys.*, **55**, 456 (1971). ^j References 12, 14b. ^k Y. T. Lee, J. D. McDonald, P. R. Le Breton, and D. R. Herschbach, *J. Chem. Phys.*, **49**, 2447 (1968); **51**, 455 (1969). ^l C. C. Rankin and W. H. Miller, *J. Chem. Phys.*, **55**, 3150 (1971). ^m D. D. Parrish and R. R. Herm, *J. Chem. Phys.*, **51**, 5467 (1969); **54**, 2518 (1971). ⁿ S. M. Freund, G. A. Fisk, D. R. Herschbach, and W. Klemperer, *J. Chem. Phys.*, **54**, 2510 (1971); H. G. Bennewitz, R. Haerten, O. Klais, and G. Müller, *Chem. Phys. Lett.*, **12**, 335 (1971); S. J. Riley, Ph.D. Thesis, Harvard University 1970. ^o J. M. Parson and Y. T. Lee, *J. Chem. Phys.*, **56**, 4658 (1972). ^p A. Schultz, H. W. Cruse, and R. N. Zare, *J. Chem. Phys.*, **57**, 1354 (1972). ^q H. J. Loesch and D. Herschbach, private communication.

ΔE of collision energy spread. Hence in most cases it is sufficient to give a statistical treatment of all the open channels coupled to each resonance r . We follow here the treatment by Miller,¹² based on our equations.

Relevant quantities are the averages with respect to the energy spread density $\rho(E)$. In particular one has

$$\langle |S_{\lambda\lambda'}|^2 \rangle_{av} \cong P_{\lambda\lambda}^{(0)} + p_{\lambda'r} p_{r\lambda} / P_r \quad (15)$$

where, for an isolated resonance

$$p_{\lambda'r} = p_{r\lambda} = 2\pi [(S_{00}^{(d)})^{1/2} c_{0r}]^2 \rho(E_r) \quad (16)$$

is a transmission probability for $\lambda \rightarrow r$, $P_r = \sum_{\lambda} p_{\lambda'r}$ is the total transmission probability, and $P_{\lambda\lambda}^{(0)}$ is the nonresonance transition probability, including the direct process and its interference with the resonance process, so that from probability conservation

$$p_{\lambda'r} + \sum_{\lambda'} P_{\lambda\lambda'}^{(0)} = 1 \quad (17)$$

A similar separation of nonresonance and resonance effects may be carried out in the angular distributions, to obtain $B_L = B_L^{(0)} + B_L^{(r)}$. The resonance part $B_L^{(r)}$ contains double sums over many pairs of

initial (and similarly of final) open channels with different orbital angular momenta l . Assuming that crossed-terms statistically cancel, one gets eq 18 for

$$\langle B_L^{(r)}(n'l', nj) \rangle_{av} \cong \frac{1}{4} (-1)^{j+j'} \sum_{JL} (p_{\lambda'r}^J p_{r\lambda}^J / P_r) \times Z(lJlJ, jL) Z(j'J'l'J, j'L) \quad (18)$$

L even and $B_L^{(r)} = 0$ for L odd, with the Z standing for algebraic coefficients which are defined in collision theory.¹³

As a consequence only even-order Legendre polynomials appear in the resonance terms, and the corresponding angular distribution in eq 14 is symmetric around $\Theta = 90^\circ$. Depending on the relative value of the nonresonance contribution we may expect a more or less pronounced symmetry, so that its magnitude could provide insight into the collision mechanism.

Table II presents some of the atom-molecule systems where formation of long-lived states appears established (atom-atom and molecule-molecule sys-

(12) W. H. Miller, *J. Chem. Phys.*, **52**, 543 (1970).

(13) (a) A. R. Edmonds, "Angular Momentum in Quantum Mechanics," Princeton University Press, Princeton, N. J., 1960, p 97; (b) J. M. Blatt and L. C. Biedenharn, *Rev. Mod. Phys.*, **24**, 258 (1952); (c) see A. M. Arthur and A. Dalgarno, *Proc. Roy. Soc., London, Part A*, **256**, 540 (1960), for applications to atom-molecule collisions.

tems have not been included). Among the nonreactive pairs, those numbered 1 to 5 are readily described in the terms presented above. Since the atom in these cases is a noble gas, there is little electronic charge rearrangement, and weak coupling predominates. With the exception of (5), where classical trajectories were employed, these systems have been calculated quantum mechanically. In the systems 6, first studied by Ham and Kinsey, we expect a considerable change in electronic structure and many open channels, so that a treatment using adiabatic potentials and statistical averages would very likely be necessary.

A large number of the listed reactive pairs have been investigated by Herschbach and collaborators. Systems 1, in which an ionic bond is broken and another one formed, are the best established examples of reactions mediated by compound states. They have been discussed in terms of statistical models that assume symmetric-top compound states broadening up along their symmetry axis, with prolate tops giving forward-backward peaking in the c.m. frame, and oblate tops peaking at about 90° . In most cases the measured angular distributions indicate prolate tops, one exception being system (5), interpreted in terms of an oblate-top compound state. In the more recently studied systems 7 and 8, Cs + SF₄ appears particularly interesting in that it has tentatively been discussed as a mixed case with both prolate and oblate-top symmetries. Systems 2 and 3 are examples where both resonance and nonresonance processes may contribute to the angular distributions, a situation described in terms of "osculating" complexes or compound states.

The statistical approximation outlined above may be applied to these reactions provided it is understood that the capture probability $p_{r,\lambda}$ and the decay probability $p_{\lambda,r}$ refer to two different reaction channels. They may be calculated by noticing that, *e.g.*, for decay one must have both breakup of the compound state and departure of the fragments from the reaction region. This last step has been described in detail by Light and coworkers¹⁴ for each fixed vibrational state p of the intermediate (in our case compound) state. In his approach, departure certainly occurs if $l \leq l_{\max}$, where l_{\max} is the angular momentum for classical orbiting in the exit channel potential, and does not occur for $l > l_{\max}$. This would correspond in our nomenclature to determining the probability of departure from the properties of the shortest-lived exit-channel resonance. The two steps, breakup and departure, may be simultaneously described with an approach similar to the Rice-Ramsperger-Kassel-Marcus theory of unimolecular decomposition,¹⁵ which distinguishes two types of LLS: energized and transition states. In the manner outlined by Safron and Herschbach,¹⁶ the departure

probability from the transition state is obtained from classical orbiting, while breakup in the energized state is described by Kassel's probability factor for unimolecular decomposition. In our nomenclature energized and transition states correspond respectively to compound-state and exit-channel resonances. Equation 16 shows that these two are coupled, since c_{or} refers to compound-state and $(S_{oo}^d)^{1/2}$ to exit-channel resonances.

Conclusions

Computational and experimental means are available at present to study LLS of van der Waals complexes. These states provide us with a new source of information on short-range intermolecular forces and play a role in the interpretation of scattering and light-absorption processes. An extension of the formalism described above for these complexes could help to clarify our understanding of LLS in reactive collisions and in collisions with charge-transfer intermediate complexes. Scattering angular distributions may provide a wealth of information on the conformation of LLS. Detailed theoretical treatments are needed to extract from angular distributions the symmetric component contributed by LLS. A common approach may be used when statistical approaches suffice. However, dynamical approaches must yet be developed for reactive and charge-transfer events, where interactions are strong and the transition from reactant to product states through LLS is not yet well understood.

Turning to computational approaches, a great deal has been done within scattering theory by looking at resonance shapes. However, for several problems in spectroscopy and in collisions where the interference of resonance and nonresonance processes is negligible, much could be learned by concentrating on the quasi-bound states. These may be related to the bound states to which they tend in the absence of coupling, *e.g.*, by means of perturbation theory. We have recently employed the wave-operator approach to discuss resonances along these lines.^{17,18} Level shifts and widths follow from a set of two coupled equations, $E_s = f_1(E_s, \Gamma_s)$ and $\Gamma_s = f_2(E_s, \Gamma_s)$ valid for all coupling strengths. In this way, it might be possible to describe LLS making use of existing experience on the calculation of bound molecular states.

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