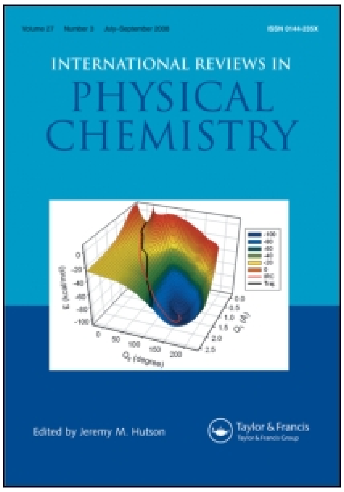

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Dynamical coupling and energy transfer in weakly bound molecular complexes†

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The existence of a special type of bound state supported by chemical forces of a different nature from those involved in traditional chemical bonds has been predicted by theory and confirmed by experiment. It is, however, only in the last decade or so that Van der Waals complexes have acquired great relevance as model systems for the study of energy flow and energy deposition during intramolecular inelastic processes. In the present analysis it is shown how even the simple event where energy is exchanged only between internal rotation and the vibrational motion along the Van der Waals (VdW) bond can lend itself to a very detailed and systematic study of the origin of the dominant dynamical couplings which drive the inelastic rearrangements. A computational example is given at the end for the case of argon and molecular nitrogen, as partners moving under the effect of a realistic interaction potential determined from several experimental data.

1. Introduction

The study of the structural properties of weakly interacting systems in the gas phase is possibly one of the best sources of information on the role that the various intermolecular forces play in guiding the relative distribution of the energy available in the thermal bath between the internal degrees of freedom of the molecular species.

When a traditional chemical bond is formed one knows that, at the temperatures of chemical interest, quite a large amount of energy will be needed to break it, and the ensuing fragments may tell us little about the internal energy distribution of the bound system before such a major perturbation occurred. On the other hand, when a weakly bound cluster of molecules is examined or when other types of Van der Waals (VdW) systems are studied, one is dealing with much weaker forces and therefore the amount of energy 'stored' in each of these bonds frequently becomes comparable with the amount of internal energy that may exist in other parts of the monomer. As a consequence of this, the weakly-bound clusters can undergo dissociation simply by internal redistribution of fairly small amounts of energy. The complex can therefore predissociate and the resultant reduction in the lifetime of the particular excited state which has been formed leads to observable broadening of the corresponding spectroscopic lines (Levy 1981, Le Roy and Carley 1980). This particular form of predissociation can be viewed as a simple unimolecular reaction along the VdW bond, with the cluster of molecules representing a sort of 'activated' system that is capable of fragmenting to yield products with several different possible internal states. This aspect

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† This contribution is dedicated to the memory of Professor M. Simonetta.

of the process is therefore directly related to the various features of the multi-dimensional potential energy surface (PES) which is driving the motion of the nuclei and which is added locally to the relative kinetic energy of the partners at each geometry of the cluster. It also means that the individual probabilities for each of the final channels to be populated during the predissociative break-up are ultimately related to the coupling potentials which act, while the complex is not too far from its equilibrium geometry, between the motion along the dissociative coordinate (i.e. the VdW bond) and the internal motion of all the other atoms which pertain to the component 'monomers' (Le Roy and Van Kranendonk 1974).

An interesting aspect of the physical situation is that the resonant nature of the break-up process is also very reminiscent of what happens when a molecule, or an atom, collides with another molecule at very small relative kinetic energy, and translational energy can therefore be deposited into the internal degrees of freedom of either partner as a result of the dynamical coupling that takes place during the encounters. In this special sense, therefore, the predissociative properties of weakly bound clusters could be studied theoretically by treating them as 'half collision' processes, i.e. by applying the usual asymptotic boundary conditions for the total wavefunction of a scattering state only to the final channels of the system, while the initial channels are treated as bound states of the complex, having negative total energy with respect to each suitable set of isolated fragments. As a consequence of this approach, what is known about the relative efficiency of rotationally and/or vibrationally inelastic scattering processes between certain molecular partners (Faubel 1983, Gianturco and Palma 1985 b) becomes the basis for the analysis of the structural properties of the weakly bound systems that are made up of the same components as the scattering partners above.

We consider first the ways by which one can gather information on intermolecular forces between partners in the cluster and then describe the dynamical models which can be employed to deal with the relative motion of the partners. Possible, simpler quantal treatments of the outgoing scattering states are then described in detail and, in the last section, results on a specific example are reported and analysed.

2. The interaction potentials

Considerable progress has been made in recent years in determining accurate potential energy surfaces for two- and three-atom systems (Scoles 1980). The usual procedure has been the supermolecule approach, whereby the interaction energy of a complex is obtained by evaluating the total energy E^x_{AB} of the AB supermolecule via a specific method x ($x=$ SCF, CI, CEPA, MBPT etc.) and then subtracting the energy of the monomers.

$$\Delta E^x = E^x_{AB} - E^x_A - E^x_B \tag{1}$$

The difficulty with this approach arises from the errors inherent in the subtraction of the large energies of the separate fragments from the only lightly different energy of the interacting components of the supermolecule (Morokuma 1977). Several authors have resorted instead to model calculations in which the long-range region of zero overlap of the charge distributions turns out to be sufficiently well described by second-order perturbation calculations, while at short range the first-order Coulomb and exchange energies dominate the interaction and can be reliably treated by SCF calculations. The difficult intermediate region is finally described by general damping functions which simply connect the two main domains of interaction at each relative orientation of the partners (Tang and Toennies 1978, Ahirichs *et al.* 1977).

In recent years, we have found it very effective to analyse several data obtained, for example, from molecular beam scattering experiments, from the spectroscopy of the bound states of the supermolecule, from bulk data like virial coefficients and transport properties, and to try to fit all these available quantities with one simple form of anisotropic potential (Gianturco *et al.* 1982, 1983, 1984, 1985 a, b). This type of multi-property analysis has the interesting advantage of allowing close interplay between the separate theoretical models employed to generate the required observable and corresponding form of that region of the full PES which is mostly responsible for its behaviour. For instance, one can associate very directly the values of the diffusion and viscosity coefficients produced by a given anisotropic potential over a wide range of temperature for a specific gaseous mixture (e.g. $He + N_2$ or $Ar + O_2$) with the shape of the effective, spherical potential at the onset of its repulsive region and with the location in space of that repulsive wall (Gianturco and Venanzi 1987). Furthermore, the interference oscillation observed experimentally in the differential cross sections, total and partial, at low collision energies ($20\,\text{meV} \leqslant E \leqslant 100\,\text{meV}$) can be interpreted and reproduced only when the relative position, depth and orientational dependence of the attractive well is established with a rather high level of accuracy (for example Gianturco and Palma (1985)). An indirect test on the reliability of such an approach was carried out through the analysis of experimental data on Ar–O_2 mixtures, where measured partial inelastic differential cross-sections were able to indicate in which direction one should modify the well anisotropy and long-range anisotropy obtained from integral cross-sections in order to reproduce the observed angular distributions of the inelastic processes (Faubel and Kraft 1986).

The infra-red spectra of the corresponding Ar–N_2 complexes seem to indicate that these VdW molecules possess orientationally localized (librational) states as well as nearly free internal rotation states (Henderson and Ewing 1974), and therefore such partners provide a system on which the dynamical coupling between different internal motions, and the corresponding flow of energy between them that can occur during the motion, can be analysed.

It is important to keep in mind that the object of the present study is to clarify structures, i.e. to assess the relative mobility of the various fragment nuclei within a VdW complex, a property which varies considerably as the various partners are changed. One observes, for instance, at one end the nearly free internal rotation of H_2 in H_2–X dimers, which are thus best described by using a basis of free rotor functions for both the potential and the vibrational wavefunctions (Le Roy and Carley 1980), while at the other end one could observe VdW complexes in which the partner molecule is strongly nonspherical and of such dimensions as to be, along one or two of them, larger than the main VdW coordinate with the rare gas; internal rotations are then strongly prevented as at specific angles (and/or distances) the full potential surface could even become infinitely repulsive. This behaviour has been found to hold for systems like anthracene–Ar or fluorene–Ar (Meerts *et al.* 1984), where one has to use a different set of internal coordinates and basis functions for the internal motion.

For all the intermediate situations it becomes necessary to select the most effective representation of the states of the complex and/or of the monomer in order to obtain a simple and reliable picture of the dynamical coupling that occurs between the nuclear motions controlled by the strong chemical bonds existing within each monomer and the overall nuclear motion that depends on the new VdW bond.

3. The dynamical models

3.1. *System hamiltonian*

We confine this study to the theory of bound triatomic molecules. The six independent variables of the ABC system in the centre-of-mass (c.m.) frame are chosen as R, r, γ, ϕ_R, θ_R and ϕ_r. The vector **R** defines the A to BC c.m. separation (or VdW coordinate), **r** the B to C separation (or molecular coordinate) and γ is the angle between these two vectors. The remaining variables are Euler angles of rotation, with (ϕ_R, θ_R) defining the orientation of **R** relative to a space fixed (SF) coordinate system and ϕ_r, the rotation of the ABC triangle about **R**.

By making use of the above coordinates we can write the ABC hamiltonian, in a.u., in the following way:

$$\mathscr{H}(\mathbf{R},\mathbf{r})=-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}-\frac{1}{2m}\frac{\partial^2}{\partial r^2}+\frac{\mathbf{l}^2}{2\mu R^2}+\frac{\mathbf{j}^2}{2mr^2}+V(R,r,\gamma) \tag{2}$$

where μ is the triatomic reduced mass, m the reduced mass of the diatomic fragment, $\mathbf{l}^2$ is the orbital and $\mathbf{j}^2$ the internal angular momentum operators squared and V is the full PES for all internal coordinates. In the case of a rigid, rotating diatomic partner BC, the needed hamiltonian and PES are further reduced as follows:

$$\mathscr{H}(\mathbf{R},\hat{r})=-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+\frac{\mathbf{l}^2}{2\mu R^2}+B_e\mathbf{j}^2+V(R,\gamma)=-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+U(R,\gamma) \tag{3}$$

where B_e is now the rotational constant for the diatom BC. The problem we wish to solve is the eigenvalue equation

$$\{E_i-\mathscr{H}(\mathbf{R},\hat{r})\}\Psi(E_i|\mathbf{R},\hat{r})=0 \tag{4}$$

where both discrete and continuum eigenvalues need to be considered. To simplify (4) one usually works in the total $\mathbf{J}^2$ representation, where

$$\mathbf{J}=\mathbf{j}+\mathbf{l} \tag{5}$$

which then allows one to write down the orbital angular momentum squared as

$$\mathbf{l}^2=(\mathbf{J}-\mathbf{j})^2=\mathbf{J}^2+\mathbf{j}^2-2\Omega^2-2\mathbf{J}_x\cdot\mathbf{j}_x-2\mathbf{J}_y\cdot\mathbf{j}_y \tag{6}$$

where $\hat{x}$ and $\hat{y}$ (mutual perpendicular) are body fixed (BF) directions orthogonal to $\hat{R}$. The helicity operator $\mathbf{\Omega}$ is defined as

$$\mathbf{\Omega}\equiv\hat{R}\cdot\mathbf{J}=\hat{R}\cdot\mathbf{j} \tag{7}$$

The eigenfunctions of $\mathscr{H}$ in the helicity (BF) representation can now be written as

$$\Psi(E_i, JM\lambda|\mathbf{R},\hat{r})=\left(\frac{2J+1}{8\pi^2}\right)^{1/2}\mathscr{D}^J_{\lambda M}(\phi_R,\theta_R,\phi_r)\cdot f(E_i, J\lambda R)/R \tag{8}$$

where λ and M are the eigenvalues of $\mathbf{\Omega}$ and $\mathbf{J}_z$, respectively, and $\mathscr{D}^J_{\lambda M}$ are rotation matrices (see for example Gianturco (1979)). It is worth mentioning at this point that the centrifugal sudden (CS) (McGuire and Kouri 1974) or the helicity decoupling approximation (HDA) (Tamir and Shapiro 1975) amount to neglecting the last two terms in equation (6), i.e.

$$\mathbf{J}_x\cdot\mathbf{j}_x+\mathbf{J}_y\cdot\mathbf{j}_y\simeq0 \tag{9}$$

However, if this approximation is not introduced, the use of expansion (8) into equation (4) leads to the well-known set of coupled equations of collision theory:

$$\left\{-\frac{1}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2}+U(a',a',J|R)-E_i^J\right\}\cdot f(E_i^J,J,a'|R)=-\sum_{a''}U(a',a'',J|R)f(E_i^J,J,a''|R) \quad (10)$$

where U are the matrix elements of the internal motion (angular) functions with the operator $U(R,\gamma)$ of equation (3). In either the SF or the BF angular basis, the coupling matrix elements are defined for each $|J\rangle$ state of the triatomic complex and the rotational predissociation (RP) processes can be fully discussed in terms of the solutions of equation (10).For the case in which the predissociating state of the VdW complex can be treated as an isolated narrow resonance, associated with a specific closed channel m, then one can make use of the full S-matrix obtained by solving equation (10) and write down the matrix element between the open channels j and j' as follows (Ashton *et al.* 1983):

$$S_{jj'}(E)=[S_d(E)]_{jj'}-i\,g_{mj}g_{mj'}/(E-E_m+i\Gamma_m/2) \quad (11)$$

where E_m is the energy of the resonance, Γ_m its total width, and g_{mj} is a complex number which is related to a partial width $\Gamma_{mj}=|g_{mj}|^2$ that determines the flux of dissociation products into the specific channel j. $[S_d(E)]_{jj'}$ represents a contribution to the S-matrix element that varies slowly with energy and is due to direct break-up without involving channel m. One can then characterize a given predissociation level by performing close-coupling scattering calculations for a suitable range of energies surrounding the expected resonance position, and by determining the resonance parameters by simultaneous least-square fits of the resulting S-matrix elements to the form of equation (11). The quality of the ensuing fit therefore provides a measure of the validity of the narrow resonance approximation and of the accuracy achieved in the convergence of the coupled solution of equation (10).

Because of the numerical complexity and size of equation (10) which may need to be solved at several energies in order to follow the above procedure, it has been much more common to resort first to approximate methods to treat the dynamical coupling and then to test them, if possible, against some specific resonance positions obtained through the more general and 'exact' CC procedure.

3.2. *Approximate procedures*

The most common way to reduce the computational efforts implied by equation (10) has always been to find a suitable partition of the full hamiltonian (Le Roy 1984). The first of these parts, say $\mathscr{H}_0$, usually provides a zeroth order description of the dynamics of the system and therefore its eigenvalues constitute estimates of the energies of all the needed bound and metastable states. The remainder of the original hamiltonian, usually called $\mathscr{H}'=\mathscr{H}-\mathscr{H}_0$, is then employed to couple the discrete eigenfunctions associated with the metastable levels of $\mathscr{H}_0$ to some isoenergetic continuum open channels that lead to predissociation. One can then easily see that, within the isolated narrow resonance approximation, the corresponding partial width (full width at half maximum) that describes the predissociation of the metastable state m into a specific open channel j is given by the familiar golden rule expression:

$$\Gamma_{mj}=2\pi\left|\int\Psi_m\mathscr{H}'\Psi_c\,\mathrm{d}\tau\right|^2 \quad (12)$$

where Ψ_m is the unit-normalized, bound-state eigenfunction of $\mathscr{H}_0$ associated with the complex state that is undergoing break-up and Ψ_c describes the isoenergetic continuum function of $\mathscr{H}_0$ associated with the final, open channel $|j\rangle$ of the two fragments.

To help our discussion of expansions in the following paragraphs, let us think of the full interaction $V(R,\gamma)$ as being made up of three terms

$$V(R,\gamma) \simeq V_1(R) + V_2(\gamma) + V_3(R,\gamma) \tag{13}$$

the first part being the spherical component of the potential, the second its angular dependence and the third the coupling between the two motions in the complex. One can then say that the different parts of the full potential (13) may have different importance, depending on the system, and therefore the corresponding expansion problem may lend itself to a different choice of basis functions, depending on which is the dominant contribution in partition (13).

3.3. *Diabatic expansions*

In this approach, which is usually considered to be the simplest, one essentially disregards the coupling effect of V_3 in equation (13) and the problem becomes separable. The corresponding total wavefunction could then be written as the product of two functions, one which depends only on R and the other only on the orientation γ (libration variable). This product can be further improved by replacing it with full expansion of a complete set of still separable functions. Both possibilities are discussed below.

3.3.1. *Diabatic rotational expansion* (*DRE*)

This approach was proposed a while ago (Beswick and Requeña 1980) but has only recently been applied to realistic systems (Roncero *et al.* 1986, Villarreal *et al.* 1987 a, b). The total wavefunction is written as a product of two subfunctions which each depend on one of the variables of the problem

$$\Psi^{JMp}_{\alpha,v_\alpha}(\mathbf{R},\hat{r}) = \chi^{Jp}_{\alpha,v_\alpha}(R)\Phi^{JMp}_{\alpha}(\gamma) \tag{14}$$

where J and M are the quantum numbers defined before, p is the parity index: $p=(-)**(J+j+l)$. The indices α and v_α refer to the quantum numbers associated with the angular (bending) and radial (stretching) motion within the complex. The function Φ belongs to a complete orthonormal set of angular basis functions defined in either the BF or SF frame of reference. Because of the presence of only *one* set of channel indices then the radial function χ is the solution of a one-dimensional, decoupled equation in which an effective potential appears

$$\left\{-\frac{1}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + V^{\alpha\alpha,\mathrm{Jp}}_{\mathrm{eff}}(R)\right\}\chi^{Jp}_{a,v_\alpha}(R) = E_{\alpha,v_\alpha}\chi^{Jp}_{a,v_\alpha}(R) \tag{15}$$

where the V_{eff} is defined by averaging over the angular function Φ

$$V^{\alpha\alpha,Jp}_{\mathrm{eff}}(R) \simeq \left\langle \Phi^{JMp}_{a} \middle| \frac{\mathbf{l}^2}{2\mu R^2} + B_{\mathrm{e}}\mathbf{j}^2 + V_1 + V_2 \middle| \Phi^{JMp}_{a} \right\rangle \tag{16}$$

To solve equation (15) to obtain both bound and metastable eigenfunctions means that all diagonal matrix elements $U(a', a'', J|R)$ of equation (10) are considered negligible with respect to the diagonal element of equation (16), hence no coupling exists between the various bound and metastable states through the mixing of R-motion and γ-motion within the complex. When this is not the case, one then obtains inaccurate estimates of the E_α values and of their corresponding Γ_α, since the angular coupling will only appear in the golden rule expression of equation (15) and not when obtaining the wavefunctions of expansion (14). One further step could thus be made by employing *all* the separate solutions of equation (15) to generate the full wavefunction of the complex.

3.3.2. *DR expansion plus configuration interaction* (*DRCIE*)

When the systems under study appear to support several bound and metastable states, it could be convenient to retain the diabatic separation of variables but to improve its representation by allowing the interaction between the states in question to be switched on. Thus, from equation (14)

$$\Psi_n^{JMp}(\mathbf{R}, \hat{r}) = \sum_{\alpha, v_\alpha} C^n_{\alpha, v_\alpha} \chi^{Jp}_{av_\alpha}(R) \Phi^{JMp}_\alpha(\gamma) \tag{17}$$

where the summation extends over all the bound states supported by each V_{eff} potential, as defined in equation (16). The functions on the r.h.s. of equation (17) can be used to construct a matrix representation of the hamiltonian (13)

$$H^{JMp}_{av_\alpha;\alpha' v_{\alpha'}} = \left\langle \Psi^{JMp}_{a, v_\alpha} | \mathscr{H} | \Psi^{JMp}_{a', v_{\alpha'}} \right\rangle = E_{\alpha, v_\alpha} \cdot \delta_{\alpha\alpha'} \cdot \delta_{v_\alpha v_{\alpha'}} + \left\langle \chi^{Jp}_{a, v_\alpha} | V^{\alpha\alpha', Jp}_{\text{eff}} | \chi^{Jp}_{a', v_{\alpha'}} \right\rangle (1 - \delta_{\alpha\alpha'}) \tag{18}$$

By diagonalization of the full matrix one can obtain new eigenvalues E_n and eigenstates $|n\rangle$ for the complex system. In some cases this turns out to be of very limited help, because each effective potential supports only a small number of discrete levels, and it does so only for the lower-lying rotational levels of the diatom. Hence the CI correction is only a small effect and all the limitations of the DR expansion are still present (Villarreal *et al.* 1987 a, b).

3.3.3. *Diabatic stretching expansion* (*DSE*)

Because of the complete separation between vibrational and librational motions implied by the diabatic expansions it becomes only a matter of expediency to decide which variable should be averaged out first. Thus, one could also consider the possibility of producing the total wavefunction from the expansion

$$\Psi^{JMp}_{v, \alpha_v}(\mathbf{R}, \hat{r}) = \Phi^{JMp}_{v, \alpha_v}(\gamma)\, \chi_v(R) \tag{19}$$

where the angular functions are obtained for each v-channel by solving an equation which is averaged over the stretching functions, each of which is in turn a solution of the eigenvalue equation

$$\left\{ -\frac{1}{2\mu} \frac{\mathrm{d}^2}{\mathrm{d}R^2} + V_1(R) \right\} \chi_v(R) = E_v \chi_v(R) \tag{20}$$

where the spherical part of the full PES is explicitly used to obtain the zeroth-order stretching functions. Thus we can write the ensuing equation, with the χ-averaged hamiltonian, for each stretching channel v

$$\left\{ B_{\mathrm{e}} \mathbf{j}^2 + E_v + \left\langle \chi_v \left| \frac{1}{2\mu R^2} \right| \chi_v \right\rangle \mathbf{l}^2 + \langle \chi_v | V_2 + V_3 | \chi_v \rangle \right\} \Phi^{JMp}_{v, \alpha_v}(\gamma) = E_{v, \alpha_v} \Phi^{JMp}_{v, \alpha_v}(\gamma) \tag{21}$$

One could then solve equation (21) by expanding the functions over a chosen set of orthonormal angular basis functions (e.g. those obtained in the expansion (17)). The above procedure includes more accurately the angular coupling than the previous expansion over angle-averaged eigenfunctions, but its final performance in correctly generating RP energies and widths strongly depends on the reliability of the χ functions: for a mildly anisotropic PES, the eigensolutions of equation (20) constitute a very good starting point for describing stretching motion, and therefore the angular basis will likewise be satisfactory. On the other hand, when the E_v are very different from the correct stretching eigenvalues, then the complete wavefunctions will also fare poorly in the angular variable and in its description of librational motion.

3.3.4. *DS plus configuration interaction* (*DSCIE*)

The most direct and simple improvement over the approximate expansion of before is again given by correcting for the potential coupling between diabatic states and therefore by modifying equation (19) as follows

$$\Psi_n^{JMp}(\mathbf{R},\hat{r})=\sum_{v,\alpha_v} c^n_{v,\alpha_v}\,\Phi^{JMp}_{v,\alpha_v}(\gamma)\,\chi_v(R) \tag{22}$$

which produces, as in the case of DRCIE of equation (18), the following representation of the full hamiltonian

$$H^{JMp}_{v\alpha_v;v'\alpha_{v'}}=\langle\Psi^{JMp}_{v,\alpha_v}|\mathscr{H}|\Psi^{JMp}_{v,\alpha_v}\rangle=E_{v,\alpha_v}\cdot\delta_{vv'}\cdot\delta_{\alpha_v\alpha_{v'}}+\langle\Phi^{JMp}_{v\alpha_v}|U_{vv'}|\Phi^{JMp}_{v'\alpha_{v'}}(1-\delta_{vv'}) \tag{23}$$

where the angle-dependent potential is written as

$$U_{vv'}(\gamma)=\left\langle \chi_v\left|\frac{\mathbf{l}^2}{2\mu R^2}+V_2+V_3\right|\chi_{v'}\right\rangle \tag{24}$$

and the χ_v are obviously solutions of the radial equation (20) for the spherical component of the interaction. The coupling between diabatic levels that is brought in by the $U_{vv'}$ potential terms of equation (23) will modify the wavefunctions and eigenvalues of equation (21) only if several bound states are supported by the spherical potential or/and by the angular potentials of equation (24).

3.4. *Adiabatic expansions*

In cases where the drastic separation implied by the previous expansions is not a very realistic description of internal motion within a VdW molecule it appears more reasonable to think of the total wavefunctions for the discrete and metastable states of the complex as given by the product of a function which depends on only *one* of the variables, be it either the stretching or the bending variable, and another function which depends only weakly on that variable and more markedly on the others. This approach simply tries to take advantage of the physical differences which exist between fast-motion variables and slow-motion variables (Segev and Shapiro 1985, Villarreal *et al.* 1987 b). In the following paragraphs we briefly review the models which can be used to exploit the adiabatic separation of motions in treating dynamical coupling within VdW complexes.

3.4.1. *Adiabatic angular expansion* (*AAE*)

One begins by writing the total wavefunction as a product of a radial function which only weakly depends on orientation and a purely angular function.

$$\Psi_{s,t}(\mathbf{R},\hat{r})=\phi_s(R;\gamma)\,F_{s,t}(\gamma) \tag{25}$$

The discrete eigenfunctions now depend on the quantum numbers s and l, associated with the VdW stretching and librational motions respectively. If one now assumes that the weak γ-dependence in the ϕ_s functions can be disregarded then one can write

$$\mathbf{l}^2\Psi_{s,l}=\phi_s(\mathbf{l}^2F_{s,l}) \tag{26a}$$

$$\mathbf{j}^2\Psi_{s,l}=\phi_s(\mathbf{j}^2F_{s,l}) \tag{26b}$$

which means that one can now obtain the ϕ_s functions as solutions of uncoupled one-dimensional equations for each γ value chosen at an arbitrary value:

$$\left\{-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+V(R,\gamma)\right\}\phi_s(R;\gamma)=W_s(\gamma)\,\phi_s(R;\gamma) \tag{27}$$

The full equation will then yield, after simple substitutions, the corresponding solutions for the F functions

$$\left\{-\frac{1}{4\mu}[A_s(\gamma),\mathbf{l}^2]+B_e\mathbf{j}^2+W_s(\gamma)\right\}F_{s,l}(\gamma)=E_{s,l}F_{s,l}(\gamma) \tag{28}$$

where

$$A_s(\gamma)=\langle\phi_s(R;\gamma)|1/R^2|\phi_s(R;\gamma)\rangle \tag{29}$$

and

$$[P,Q]=PQ+QP \tag{30}$$

A standard way of solving equation (28) is to expand the F functions over a BF rotational basis set (Pack 1974)

$$\begin{aligned}F_{s,l}(\gamma)&=F_{s,l}(\hat{R},\hat{r})\\&=\sum_{j\Omega}C^{s,l}_{j\Omega}\langle\hat{R},\hat{r}|JMj\Omega\rangle\end{aligned} \tag{31}$$

where the coefficients on the r.h.s. are well known products of spherical harmonics and Wigner D-matrices (Rose 1957). The representation of the $\mathbf{l}^2$ and $\mathbf{j}^2$ operators in the BF frame is also well known from the literature (Gianturco 1979) and therefore the A_s and W_s functions can also be given in terms of Legendre polynomial expansions to yield finally, by diagonalization of the coupled equations which stem from (28), the desired energies of the triatomic system and the corresponding wavefunctions via the knowledge of the coefficients in equation (31).

3.4.2. *AA plus configuration interaction* (*AACIE*)

One can improve on the previous representation of discrete solutions for the eigenstates of the triatomic complex by allowing for the full potential to couple the separate solutions of equation (25). This implies

$$\Psi_k(\mathbf{R},\hat{r})=\sum_{s,l}a^{k}_{s,l}\phi_s(R;\gamma)F_{s,l}(\gamma) \tag{32}$$

hence the usual Schrödinger equation

$$\mathscr{H}(\mathbf{R},\hat{r})\,\Psi_k(\mathbf{R},\hat{r})=E_k\Psi_k(\mathbf{R},\hat{r}) \tag{33}$$

may be solved by representing the full hamiltonian $\mathscr{H}$ in that basis and by then diagonalizing the corresponding matrix. A typical element of that matrix can therefore be written as

$$H_{sl;s'l'} = \langle F_{s,l}(\gamma)\,\phi_s(R;\gamma)|\mathscr{H}|\phi_{s'}(R;\gamma)\,F_{s'l'}(\gamma)\rangle = \langle F_{s,l}|W_s(\gamma)|F_{s,l'}\rangle\delta_{ss'}$$
$$+B_e\langle F_{s,l}\phi_s|\mathbf{j}^2|\phi_{s'}F_{s'l'}\rangle + \frac{1}{2\mu}\left\langle F_{s,l}\phi_s\left|\frac{\mathbf{l}^2}{R^2}\right|\phi_{s'}F_{s',l'}\right\rangle \quad (34)$$

If the eigenvalues of equation (27) and its eigensolutions are written as an expansion over Legendre polynomials, then

$$W_s(\gamma) = \sum_\lambda \omega_{s,2\lambda} P_{2\lambda}(\cos\gamma) \quad (35\,a)$$

$$\phi_s(R;\gamma) = \sum_k \alpha_k^s(R)\,P_k(\cos\gamma) \quad (35\,b)$$

where the case of an homonuclear diatomic fragment has been considered in equation (35 *a*). One can now obtain more explicitly all the terms appearing in equation (34) by first rewriting the elements of the basis of the expansion (32) as

$$\phi_s(R;\gamma)\,F_{s,l}(\gamma) = \sum_k \alpha_k^s(R) \sum_{j\Omega} c_{j\Omega}^{s,l} \sum_p \left(\frac{2j+1}{2p+1}\right)^{1/2} C(jkp;\Omega 0\Omega)\,C(jkp;000)\langle \hat{R},\hat{r}|JMp\Omega\rangle \quad (36)$$

as was earlier derived in more detail (Villarreal *et al.* 1987 b). Thus one can write

$$\langle F_{s,l}|W_s|F_{s,l'}\rangle = \sum_{jj'\Omega\lambda} C_{j\Omega}^{s,l} C_{j'\Omega}^{s,l'} \omega_{s,2\lambda} \langle JMj\Omega|P_{2\lambda}|JMj'\Omega\rangle \quad (37)$$

and

$$B_e\langle F_{s,l}\phi_s|\mathbf{j}^2|\phi_{s'}F_{s'l'}\rangle = B_e\Bigg\{\sum_{k,k'} \langle \alpha_k^s|\alpha_{k'}^{s'}\rangle_R$$
$$\times \sum_{jj'\Omega} c_{j\Omega}^{sl} c_{j'\Omega}^{s'l'} \times \sum_p \frac{(2j+1)^{1/2}(2j'+1)^{1/2}}{(2p+1)} C(jkp;\Omega 0\Omega)$$
$$\times C(jkp;000) \times C(j'k'p;\Omega 0\Omega) \times C(j'k'p;000)p(p+1)\Bigg\} \quad (38)$$

where $p \in [p_{\min}, P_{\max}]$ and

$$P_{\min} = \max(|k-j|;|k'-j'|)$$
$$P_{\max} = \min(k+j;k'+j'). \quad (39)$$

Finally, the last term on the r.h.s. of (34) can be rewritten as

$$\frac{1}{2\mu}\left\langle F_{s,l}\phi_s\left|\frac{\mathbf{l}^2}{R^2}\right|\phi_{s'}F_{s'l'}\right\rangle = \frac{1}{2\mu}\Bigg\{\sum_{k,k'}\left\langle \alpha_k^s\left|\frac{1}{R^2}\right|\alpha_{k'}^{s'}\right\rangle$$
$$\times \sum_{j\Omega}\sum_{j'}\sum_{\Omega'=\Omega-1}^{\Omega+1} C_{j\Omega}^{s,l} c_{j'\Omega'}^{s'l'} \sum_p \frac{(2j+1)^{1/2}(2j'+1)^{1/2}}{2p+1}$$
$$\times C(jkp;\Omega 0\Omega)\,C(jkp;000) \times C(j'k'p;\Omega' 0\Omega')$$
$$\times C(j'k'p;000)\langle JMp\Omega|\mathbf{l}^2|JMp\Omega'\rangle\Bigg\} \quad (40)$$

3.4.3 *Adiabatic stretching (best local) expansion (ASE)*

Having discussed the situation where the angular motion is considered to be the slow one with respect to the motion along the VdW radial coordinate, it is of interest to examine the other possible situation, i.e. the fast motion along the librational coordinate with a relatively slow motion along the stretching coordinate. We solve, at each R value, the equation

$$\left[V(R,\gamma)+B_e\mathbf{j}^2+\frac{\mathbf{l}^2}{2\mu R^2}\right]g_l(\hat{R},\hat{r};R)=U_l(R)\,g_l(\hat{R},\hat{r};R) \tag{41}$$

where l represents the librational (angular) quantum number. One begins by expanding the g's in a BF angular basis set and by determining the coefficients by diagonalization

$$g_l(\gamma;R)=\sum_{j\Omega}G^l_{j\Omega}(R)\langle\hat{R},\hat{r}|JMj\Omega\rangle \tag{42}$$

The full wavefunction for the discrete states is written down as a simple product

$$\Psi_{s,l}(\mathbf{R},\hat{r})=g_l(\gamma;R)\Phi_{s,l}(R) \tag{43}$$

and one has to assume the adiabatic condition by saying that

$$-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}=T_R\quad\therefore\quad T_R(g\cdot\Phi)\simeq g(T_R\Phi) \tag{44}$$

hence the radial functions are given as solutions of the equation

$$[T_R+U_l(R)]\Phi_{s,l}(R)=E_{s,l}\Phi_{s,l}(R) \tag{45}$$

which is entirely equivalent to what was written for the angular variable in equation (28). Here the effective potential U_l is defined in equation (41). It is clear from its definition that

$$U_l(R)\underset{R\to\infty}{\sim}B_e j(j+1) \tag{46}$$

which implies that the local, librational quantum number l becomes asymptotically the rotational quantum number of the isolated diatom.

The usefulness of this type of adiabatic expansion is related to the degree of validity of equation (44), i.e. to the possibility that the angular motion of the diatomic fragment be largely decoupled from the stretching motion of the rare-gas atom in the complex. H_2–Ar and HD–Ar appear as possible candidates for such behaviour (Hutson and Le Roy 1983), while the example that we give below pertains to a more intermediate class of weakly bound complexes, i.e. to those for which the internal rotation is partially hindered by the stretching motion of the rare-gas atom.

3.4.4. *AS plus configuration interaction expansion (ASCIE)*

To complete the treatments discussed in this review, we examine the case in which the best local angular representation, at each fixed R value, is improved by allowing the full potential to couple the discrete eigenfunctions of the previous paragraph.

The general problem is again that of writing down the matrix representation of the full $\mathscr{H}$ of equation (3) over the AS basis of equation (43). One can then write each of them as follows

$$H_{sl,s'l'} = \langle \phi_{s,l}(R)\, g_l(\gamma; R) | T_{\mathrm{R}} + V(R,\gamma) + B_{\mathrm{e}}\mathbf{j}^2 + \frac{\mathbf{l}^2}{2\mu R^2} | g_{l'}(\gamma; R)\, \phi_{s'l'}(R) \rangle$$

$$= \left\langle \phi_{s,l} g_l \right| - \frac{1}{\mu} \frac{\partial g_{l'}}{\partial R} \frac{\partial \phi_{s'l'}}{\partial R} \left. \right\rangle + \left\langle \phi_{sl} g_l \right| - \frac{1}{2\mu} \frac{\partial^2 g_{l'}}{\partial R^2} \phi_{s'l'} \left. \right\rangle + E^{s,l} \delta_{ss'} \delta_{ll'} \tag{47}$$

If one now defines the quantity

$$F_{ll'}(R) = \left\langle g_l \left| \frac{\partial g_{l'}}{\partial R} \right. \right\rangle_{\gamma} \tag{48}$$

and remembers that

$$\left\{ V + B_{\mathrm{e}} \mathbf{j}^2 + \frac{1}{2\mu} \frac{\mathbf{l}^2}{R^2} \right\} \frac{\partial g_l}{\partial R} = U_l(R) \frac{\partial g_l}{\partial R} U_l'(R) g_l - \frac{\partial V}{\partial R} g_l + \frac{1}{4\mu R^3} \mathbf{l}^2 g_l \tag{49}$$

then it is easy to show that

$$F_{l,l'}(R) = \frac{1}{U_{l'}(R) - U_l(R)} \left\{ \left\langle g_l \left| \frac{\partial V}{\partial R} \right| g_{l'} \right\rangle - \frac{1}{4\mu R^3} \langle g_l | \mathbf{l}^2 | g_{l'} \rangle \right\} = 0 \qquad \text{if } l = l' \tag{50}$$

The problem of evaluating matrix elements like that of equation (47) is transformed into the search for a suitable representation for the $F_{l,l'}$ functions of equation (50), which will act on the purely radial basis employed in the expansion (43).

3.5. *Golden rule matrix elements*

As already mentioned in section 3.2 all the various approximate procedures discussed in sections 3.3 and 3.4 are ultimately employed to evaluate the 'golden rule' matrix elements of equation (12). To better illustrate this point, we will describe here the evaluation of the channel halfwidths for the angular adiabatic expansion (AAE) of section 3.4.1.

If one employs the familiar Infinite Order Sudden (IOS) approximation to obtain the full continuum functions for the breaking-up of the VdW complex (Secrest 1975), one can write down the expression

$$\Psi_{j,\Omega,\varepsilon,\bar{l}}(\mathbf{R}, \hat{r}) = \Phi_{\varepsilon,\bar{l}}(R; \gamma) \langle \hat{R}\, \hat{r} | JMj\Omega \rangle \tag{51}$$

where the ϕ are energy normalized solutions for a given choice of arbitrary angular momentum $\bar{l}$, of the following γ-dependent equation

$$[T_R + V(R,\gamma)] \phi_{\varepsilon,\bar{l}=0}(R; \gamma) = \varepsilon \phi_{\varepsilon,\bar{l}=0}(R; \gamma) \tag{52}$$

where the $\bar{l} = 0$ case has been considered for simplicity and where ε gives the kinetic energy of the fragments for the case where the energy of the continuum state is given 'on the energy shell' by the usual expression

$$E(j) = \varepsilon + B_{\mathrm{e}} \cdot j(j+1) \tag{53}$$

The RP halfwidth associated to a metastable state of the complex, labelled by the discrete quantum numbers $|s, l\rangle$, can now be estimated by the expression

$$\Gamma_{s,l} = \Pi \sum_{j\Omega} | V^{d\to c}_{sl\to j\Omega} |_2 \tag{54}$$

where each of the discrete-continuum ($d\to c$) coupling matrix elements is given by

$$V^{d\to c}_{sl\to j\Omega} = \langle \Psi_{j\Omega,\varepsilon,\bar{l}} | \mathscr{H}' | \Psi_{s,l} \rangle \tag{55}$$

and the involved wavefunctions are those defined by equations (51) and (25), respectively. The additional coupling operator includes the effects of fragment rotational and relative orbital angular momentum operators. Its explicit expression has been worked out in detail by us (Villarreal *et al.* 1987 b) and will not be repeated here. The final expression for the halfwidths becomes more complicated when the AACIE model is employed, since we now have (as can be seen from equation (32) and following)

$$\Gamma_k = \Pi \sum_{j\Omega} |U^{d\to c}_{k\to j\Omega}|^2 \tag{56}$$

where

$$\begin{aligned} U^{d\to c}_{k\to j\Omega} &= \langle \Psi_{j\Omega,\varepsilon,\bar{l}} | \mathscr{H}' | \Psi_k \rangle \\ &= \sum_{s,\,l} a^k_{s,l} \langle \Psi_{j\Omega,\varepsilon,\bar{l}} | \mathscr{H}' | \Psi_{s,l} \rangle \end{aligned} \tag{57}$$

but now the continuous energy at the resonance, ε, is given by $E_k - B_e j(j+1)$ and therefore the summation on the r.h.s. of equation (57) is only apparently a linear combination of the matrix elements of equation (55), as none of the $E_{s,l}$ of equation (28) even coincides with the E_k of equation (33).

4. A computational example

The interaction of heavy rare gases like argon with diatomic targets corresponding to many electron systems (e.g. beyond the H_2 example) constitutes an interesting case study for the dynamical couplings that we have discussed in the previous sections. For the Ar–N_2 case, recent calculations of bound and metastable states of the complex have been carried out by Brocks and Van der Avoird (1987) by an exansion in a basis set which consists of products of free rotor angular functions and radial basis functions. The expansion parameters were then variationally optimized by a method already employed for other systems (Tennyson and Van der Avoird 1980). They adopted an approximate procedure to evaluate resonance positions and also obtained from it the corresponding widths of the metastable states by a model calculation of the corresponding phase shifts around the energy positions obtained by the first step of calculations (Brocks 1987, Grabenstetter and Le Roy 1979). Since they employed the same anisotropic potential that we discussed in section 2, it would be interesting to see how well our present methods compare with the more time-consuming calculations employed by the above authors.

Table 1 presents the bound states obtained with the rotational diabatic and adiabatic methods discussed in the previous sections. In both cases the configuration interaction correction is also employed. One sees that for the example chosen, as it supports a fair number of bound states, the correction to the eigenvalues introduced by the CI calculations is considerable, as opposed to what was found in lighter systems with fewer bond states for the complex and for which two or three quanta of internal rotation were sufficient to eliminate all bound states (Villarreal *et al.* 1987 b). The calculations labelled BVdA (Brocks and Van der Avoird 1987) show fairly good agreement with the AACI results, although they are only referring to $j=0$ internal

Table 1. Bound states and associated rotor states for the Ar–N_2 VdW complex. Total angular momentum $J=0$ and even rotor states only. The present results are labelled by the acronyms discussed in the main text. The energy scale is in cm^{-1}.

DRE/*j*		DRCIE/*j*		AAE/*j*		AACIE	BVdA†
−71·20	0	−76·72	0	−78·33	0	−78·001	−77·95
−52·77	2	−55·04	2	−54·52	2	−56·255	−56·17
−46·81	0	−46·97	0	−51·53	0	−48·363	—
−30·10	2	−35·30	2	−31·68	0	−37·265	−37·17
−28·66	0	−28·35	0	−31·55	2	−29·382	—
−24·25	4	−21·98	4	−27·48	4	−23·287	—
−15·56	0	−17·98	0	−17·35	0	−19·900	−19·74
−13·33	2	−11·69	2	−14·62	2	−12·387	—
−6·95	0	−7·25	0	−7·88	0	−9·724	−9·53
−2·23	0	−4·76	2	−3·89	4	−6·077	—
−1·56	4	−2·50	0	−2·37	2	−2·927	−2·81
−1·37	2	−0·45	0	—		−0·704	−0·64
−0·34	0						

† From Brocks and Van der Avoird (1987).

states (or, rather to $l=0$ librational states) and therefore cannot be easily related to a CI calculation. The present methods also indicate that a free-rotor picture of N_2, rotationally excited to $j=4$, is still giving rise to bond complexes.

When one carries out a rigorous dynamical calculation, the S-matrix elements indicate the presence of isolated narrow resonances, as discussed in section 3.1, equation (11). A convenient way of expressing it is given by the familiar equation (Taylor 1972)

$$\mathbf{S}(E)=\mathbf{S}_{\mathrm{bg}}(E)\left\{\mathbf{1}-\frac{\mathrm{i}\mathbf{A}}{E-E_r+i\Gamma/2}\right\} \tag{58}$$

where $\mathbf{S}_{\mathrm{bg}}$ is the background S-matrix and R_r, Γ are respectively the position and width of a given resonance. **A** is a complex matrix related to the g_{im} quantities of equation (11) (Taylor 1972).

One can now define two energy-dependent, real functions given by

$$\mathbf{R}(E)=\sum_{k=1}^{N}\mathrm{Re}\,[(\mathbf{S}_{\mathrm{bg}}^{+}\mathbf{S})_{kk}] \tag{59 a}$$

$$\mathbf{T}(E)=\sum_{k=1}^{N}\mathrm{Im}\,[(\mathbf{S}_{\mathrm{bg}}^{+}\mathbf{S})_{kk}] \tag{59 b}$$

where Re(z) and Im(z) are respectively the real and imaginary part of the complex quantity z. Since both **S** and $\mathbf{S}_{\mathrm{bg}}$ are unitary matrices, The **R** and **T** functions assume a simple lorentzian form (Delgardo-Barrio *et al.* 1985)

$$\mathbf{R}(E)=N-\frac{\Gamma^2/2}{(E-E_r)+\Gamma^2/4} \tag{60 a}$$

$$\mathbf{T}(E)=-\frac{\Gamma(E-E_r)}{(E-E_r)^2+\Gamma^2/4} \tag{60 b}$$

where N is the number of open channels at the considered energy E. It follows that, for $E=E_r$

$$\mathbf{R}(E_r)=N-2$$

and

$$\mathbf{T}(E_r)=0 \tag{61}$$

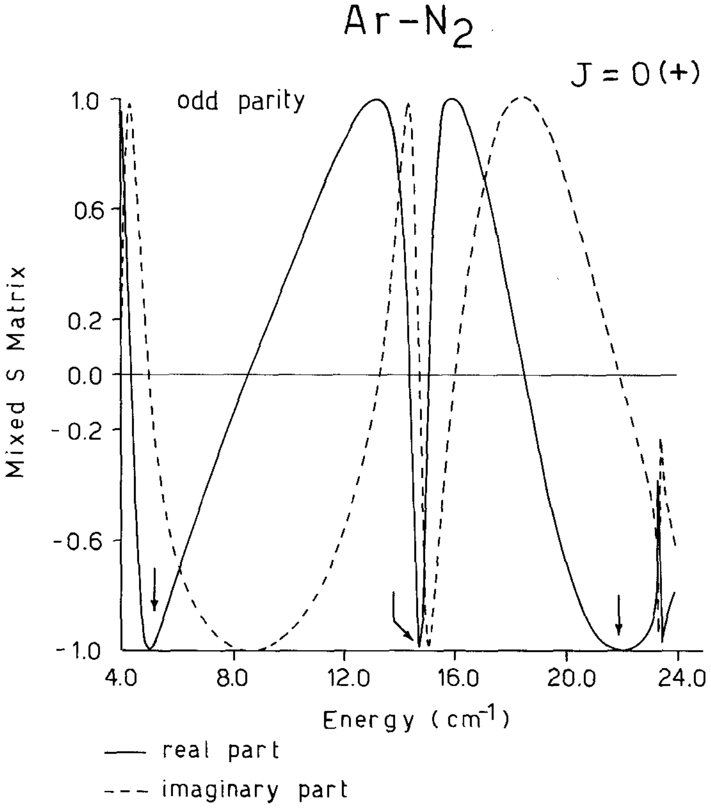
while, for

$$E=E_r\pm\Gamma/2$$

$$\mathbf{R}(E_r\pm\Gamma/2)=N-1 \tag{62}$$

and $\mathbf{T}$ $(\mathrm{E}_r\pm\Gamma/2)$ is an extremum. An example of this behaviour is given in the figure, where the **R** and **T** functions are plotted for the case of ortho-N_2 (add j values) at $J=0$ and over a range of energies where three isolated resonances are visible. The CC calculations were carried out by including rotational states up to $j=11$ and satisfactory numerical convergence was achieved on the S-matrix elements. The S_{bg}-matrix was obtained from an artificial channel calculation in which the closed channel which supports the resonance in question is omitted.

The various thresholds for the onset of continuum states of the system occur here at 3·997 cm^{-1} for the $j=1$ state, at 23·982 cm^{-1} for $j=3$ state and at 39·955 cm^{-1} for $j=5$



Computed mixed-S matrix elements (real part **R** and imaginary part **T**) for the Ar–N_2 complex at energies below the $j=3$ rotational threshold, for the $J=0$ and ortho-nitrogen cases.

state of the isolated N_2 rotor. In the figure one therefore sees that $\mathbf{R}(E)$ goes to -1 for the first resonance at $-4\,\mathrm{cm}^{-1}$, just above the first threshold, while $\mathbf{T}(E)$ goes to zero, as expected from equation (61). Both the following resonances are still below the second threshold and therefore the two functions behave exactly the same way as for the first resonance. The corresponding zeros of $\mathbf{R}(E)$ are also telling us about the width of each resonance, as indicated by equation (62). All the cases in question correspond to a physical situation in which the N_2 fragment, after the RP process, is left in the $j=0$ state, and the energy balance with the $\Delta j=1$ energy transfer from $j=1$ is provided by the relative translational energy of the fragments.

Table 2 shows the resonant states calculated with the various models discussed in this review and compares them with the exact CC results obtained as explained above. One sees that the models which include CI agree better with the exact results, as also happens with the results of Brocks and Van der Avoird (1987). On the other hand, none of the approximate approaches manages to reproduce exactly the predicted widths and positions of the CC calculations. This indicates that dynamical coupling in the chosen example requires the full presence of *both* bound–bound and bound–continuum CI as is done via the 'half-collision' approach of the exact calculations. It is, however, important to point out that angular adiabatic calculations are coming within 2–3% of the exact resonant energies and therefore provide, at little cost, a useful mapping of metastable states which can than be more accurately studied with the full dynamical coupling of the scattering equations approach.

Table 2. Metastable states and resonance partial widths for the Ar–N_2 complex. $J=0$ and even rotor states only. The acronym of each column heading is explained in the main text. The $j=2$ and 4 thresholds are $11{\cdot}99\,\mathrm{cm}^{-1}$ and $39{\cdot}97\,\mathrm{cm}^{-1}$ respectively. All quantities are in cm^{-1}.

DRE/Γ		DRCIE/Γ		AACIE	BVdA/Γ†		Exact/Γ	
6·32	1·83	2·71	0·35	0·64	1·5	0·3	1·30	0·06
10·38	0·84	7·39	1·25	4·91	1·50	0·98	5·30	2·9
11·35	0·19	10·13	0·34	8·88	7·90	1·6	7·88	0·76
—	—	11·74	0·01	11·22	11·2	0·33	11·00	0·13
—	—	—	—	11·93	—	—	11·96	0·022
15·20	3·96	15·69	4·26	—	12·7	1·7	—	—
21·06	0·03	22·67	0·26	21·82	22·60	0·38	22·20	0·20
27·14	3·02	28·33	4·18	25·82	25·90	3·5	25·56	2·97
34·75	1·86	34·36	1·51	33·10	32·30	1·4	32·30	1·11
38·69	0·82	38·33	1·28	37·75	37·80	0·64	37·43	0·34
39·99	0·14	39·92	—	38·71	40·0	0·19	39·67	0·082
				39·75				

† From Brocks and Van der Avoird (1987).

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