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Author

Frey, J.G.

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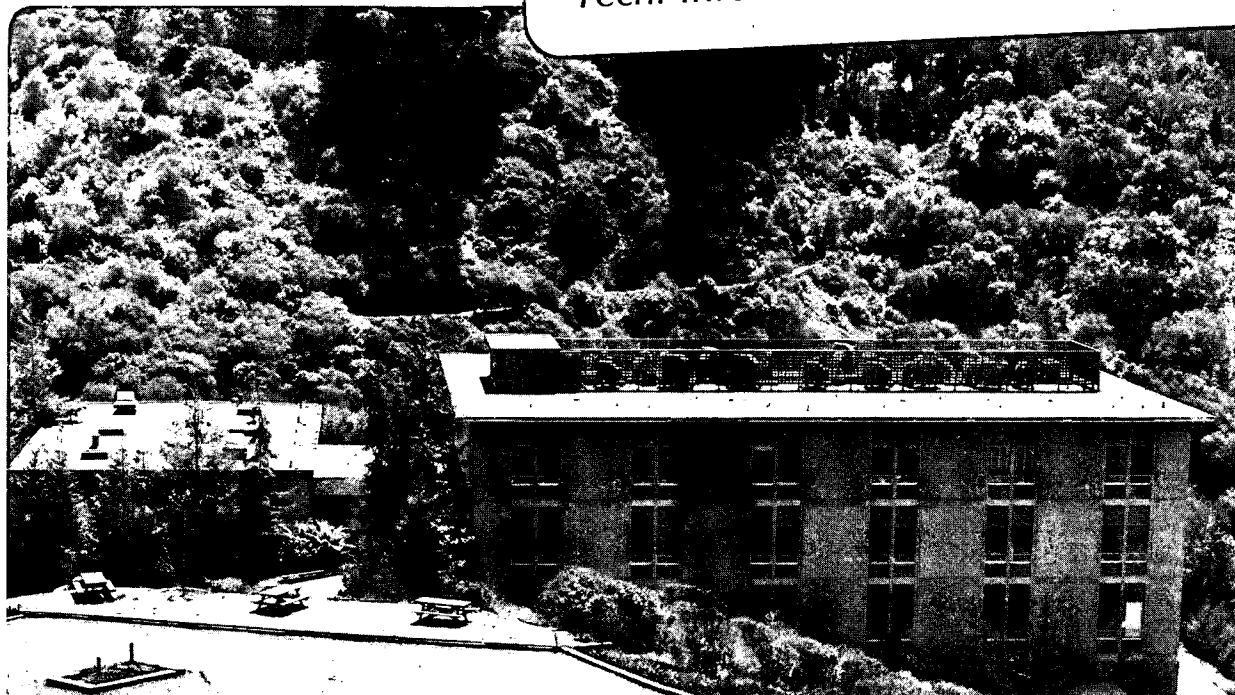
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J.G. Frey

September 1983

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Excited vibrational states near dissociation in weakly
bound triatomic systems

Jeremy G. Frey

Lawrence Berkeley Laboratory,
Materials and Molecular Research Division,
MMRD 70A-4418
University of California,
Berkeley,
California, CA 94720.
USA.

ABSTRACT

The vibrational motion of a weakly bound M_3 complex is investigated using hyperspherical coordinates and an adiabatic separation of the radial and angular motions within the molecule. It is shown that the vibrational energy levels near dissociation correlate to an M atom orbiting about a rotating M_2 core. Application is made to the neon trimer assuming an approximate pairwise additive potential.

Introduction

The appropriate form of the hyperspherical coordinates for the application to triatomic molecular systems are given by Smith[1]. In this coordinate system the three Euler angles define the molecular plane and the three internal coordinates which consist of a hyper-radius(ρ) and two "kinematic" angles (θ and ϕ) are related to the inter-nuclear distances (r_{ij}). This relationship is shown in equation (1) for the case where all three particles have the same mass. These hyperspherical coordinates are particularly advantageous in an M_3 system because they have the virtue of treating all the three particles on an equal footing.

$$r_{12}^2 = (3)^{-1/2} \rho^2 (1 + \cos 2\theta \cos 2\phi)$$

$$r_{23}^2 = (3)^{-1/2} \rho^2 (1 + \cos 2\theta \cos 2(\phi + \delta)) \quad (1)$$

$$r_{13}^2 = (3)^{-1/2} \rho^2 (1 + \cos 2\theta \cos 2(\phi - \delta))$$

$$\delta = \pi/6$$

The vibrational energy levels of a three body molecular system are determined by using the method of hyperspherical harmonics[2] in the hyperspherical coordinate system described above. This method employs the hyperspherical harmonic functions, which are the eigenfunctions of the angular part of the six dimensional Laplacian operator, as a basis set in which to expand the angular dependence of the vibrational wavefunction of the M_3 molecule. In this way the hyperspherical harmonics are the analogues to the spherical harmonics in three dimensions. To achieve a tractable calculation an adiabatic separation is made between the angular and radial motions within the molecule. The radial dependence of the wavefunction can then be calculated without the use of a basis set expansion. The use of this adiabatic separation of the angular and radial motions implicitly assumes that the nature of the angular dependence of the wavefunction depends only "slowly" on the radial coordinate. In this treatment of the excited vibrational states no attempt has been made to include the effects of the remaining non-adiabatic coupling that is neglected by the adiabatic approximation. Such treatments have been made for the ground state of both molecular and atomic systems by using a perturbation approach[3].

The neon trimer is a simple case in which all the three particles are the identical. The hyperspherical harmonic method allows the required permutational symmetry with respect to the interchange of the identical particles to be included very easily. Indeed this is a particularly advantageous feature of the method. Equation (1) shows that the coordinates θ and ρ are both symmetric to all particle permutations. If the total angular momentum of the molecule is zero, then all the information on the permutational symmetry of the molecule is contained solely in the dependence of the wavefunction. The effect of the permutations is to act as "kinematic" rotations on the angle ϕ . In the calculation presented here only the totally symmetric levels (with respect to permutation) were evaluated, because the neon atom is a boson with zero spin. The hyperspherical harmonic functions have a ϕ dependence of the form $\cos(n\phi)$ and the requiring them to be totally symmetric restricts the n to be a multiple of 3.

A large number of hyperspherical harmonic functions are required in the angular basis in order to ensure that the adiabatic channel potentials are converged at large ρ . It is one of the major difficulties with the use of the hyperspherical harmonics (rather than just the hyperspherical coordinate system) that the convergence with respect to the size of the angular basis is rather 'slow' and this becomes increasingly true at large ρ . The high permutational symmetry of the M_3 molecule does allow the size of the basis set to be considerably smaller than it would be for a general triatomic molecule.

The Potential

The potential energy surface for the M_3 molecule is built up assuming pairwise additivity. This should be a good approximation in the case of the neon trimer, since the three body term in the potential is expected to amount to less than 2% of the binding energy even at the equilibrium geometry. In this work the pair potential is represented by the sum of two gaussian terms, in the form of equation (2).

$$V(r) = \frac{\epsilon}{1-\beta} \left[\exp(-\beta^2 x^2 (r^2 - r_m^2)) - \beta^2 \exp(-x^2 (r^2 - r_m^2)) \right] \quad (2)$$

$$k = 4\beta^2 x^4 r_m^2 \epsilon$$

e - The well depth (27.5 cm^{-1})

r_m - The intermolecular separation at the minimum (3.07 \AA)

k - The force constant at $r = r_m$ ($228 \text{ cm}^{-1} \text{ \AA}^{-2}$)

β - A skewing parameter (5)

The values used for Ne_2 are shown in the parentheses. A better fit to the neon dimer pair potential has been obtained with $\beta = 2.5$ [4].

This form of the potential was chosen because it facilitates the rapid calculation of the angular matrix elements of the potential in the hyperspherical harmonic basis, since a gaussian has a simple analytic expansion in terms of the hyperspherical harmonic functions[5]. The resulting intermolecular potential has an incorrect asymptotic form, because it falls to zero at large internuclear separations too rapidly compared to that expected from the dispersion interactions. Nevertheless the general conclusions about the nature of the excited vibrational states of the trimer should be valid.

In order to solve for the angular motion at fixed rho, the "clamped rho" hamiltonian, H_{ρ} of equation (3), is diagonalized in the hyperspherical angular basis for different values of rho, ranging from 2.0 $\overset{\circ}{\text{A}}$ to 15.0 $\overset{\circ}{\text{A}}$, contained on a grid of about 20 points.

$$H_{\rho} Q(\Omega; \rho) = U(\rho) Q(\Omega; \rho) \quad (3)$$
$$H_{\rho} = (\Lambda^2 + 15/4) / \rho^2$$

$$\Omega \equiv [\theta, \phi]$$

where Λ^2 is the angular part of the Laplacian in hyperspherical coordinates [1], and $Q(\Omega; \rho)$ are the angular wavefunctions calculated for the radius fixed at the value ρ .

The eigenvalues $U(\rho)$, as a function of ρ define the so called channel potentials. In the adiabatic approximation each of these channels will give rise to an independent solution of the original Schrodinger equation, that is the channels are decoupled at this level of approximation. The interpretation of these channel functions is discussed in the next section. Within each channel the radial part of the wavefunction is obtained by solving the on dimensional Schrodinger equation by the Numerov-Cooley method. In order to obtain the potentials in a suitable form for the Numerov integration, the channel potentials are interpolated by the method of cubic splines on to an equally spaced grid containing a few hundred points. The vibrational energy levels of the trimer were calculated only for states in which the total angular momentum of the complex is zero and no rotational excitation of the complex was considered.

The vibrational energy levels

The channel potentials, $U(\rho)$ are shown in Figure 1. This figure may be interpreted as showing the variation in the "bending" energy of the complex with ρ , at least near the equilibrium geometry. Each channel provides the potential energy function for the motion along what is approximately a stretching coordinate of the complex, in a manner similar to that of a diatomic molecule, for different degrees of excitation of the bending motion. The minimum of the ground state channel occurs at a value of ρ consistent with an equilateral configuration of the complex, with the internuclear distances corresponding to the particle separations at the minimum of the dimer potential. This is confirmed by the angular average of $\cos 4\theta \approx -1$.

$$\rho_m = (3)^{1/4} r_m = 4.04 \text{ \AA}$$

The position of the minimum moves out towards larger ρ in the higher energy channels, which correspond to increasing excitation of the "bending" mode of the complex.

The separation of the lowest two channels is approximately twice the harmonic bending vibrational quantum of Ne_3 in an equilateral configuration. However the separation between adjacent channels decreases rapidly with increasing energy, which shows the highly anharmonic nature of the vibrational motion of the molecule.

The fact that the odd overtone levels of the bend are not seen (which gives rise to the $2v_b$ separation of the lowest two channels) is a consequence of the Pauli principle. This can be seen by considering the permutation-inversion symmetry of the molecule. Since all the permutation operations are "feasible" in such a weakly bound system, the relevant symmetry group is S_3 (the symmetric group of order three), which is isomorphic to the point group D_{3h} . If just the $J = 0$ levels are considered then referring to Herzberg[6], the overall vibration rotation symmetry is A_1 for a non degenerate vibrational level, but E type if it is doubly degenerate. Only the A_1 levels have the permutational symmetry that is required by the Pauli principle. For example the states with $V_b = 0$ transform as A_1 , while the states with $V_b = 1$ are degenerate and transform as E but the states with $V_b = 2$ are again non-degenerate and transform as A_1 .

This alternation of symmetry continues and gives rise to the separations between the adiabatic curves obtained above, which only pertain to the A_1 states.

The channel potentials shown in Figure 1, have asymptotic limits for large ρ which form a set of levels whose spacing increases in a manner similar to the rotational levels of a diatomic molecule. A comparison of the asymptotes obtained by extrapolating the channel potentials to large ρ , with the rotational energy levels of Ne_2 is made in Table I. Only even rotational levels of the diatomic molecule occur since Ne_2 is a homonuclear zero spin diatomic molecule. The reasonable agreement between these values shows that the channel potentials which at equilibrium correspond to excitation of the bending mode of the trimer correlate at large ρ with the rotational energy levels of the dimer. Within each channel, the vibrational stretching states, shown in Table 2, approach the the corresponding rotational energy level of the dimer, which is the dissociation limit for that channel.

Conclusion

This demonstrates that the vibrational dynamics do reflect the change in geometry as the molecule dissociates. The molecule has initially an equilateral configuration but upon excitation the geometry becomes increasingly more akin to that of an atom plus diatom system, with the M atom orbiting about a rotating M_2 core. Though this behaviour is entirely reasonable it has not been constrained on the system by the method of vibrational analysis. At large ρ , for the same value of the hyper-radius the molecule could adopt a configuration anywhere between all the particles equally (and widely) spaced or the atom-diatom limit. The lower energy channels are seen to correlate to the atom and diatom dissociation limit. The higher energy channels do tend asymptotically to zero energy, which corresponds to the reference configuration, with all the particles at infinity.

The use of the hyperspherical coordinate system together with the same adiabatic separation has been applied to two electron systems [7]. In the case of the Helium atom the adiabatic channels (in ρ) correlate asymptotically with the energy levels of the He^+ ion. This provides another example of the uniform manner in which a three body system correlates with a two body limit. The calculation of the energy of the excited and auto-ionizing states of the Helium atom by this method is greatly facilitated by this fact [8].

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Figure 1 : The adiabatic channel potentials for Neon trimer.

Table 1 : The comparison of the asymptotic limit (E_{asym}) of the adiabatic channel potentials with the vibration-rotation energy levels of Ne_2 .

Table 2 : The "stretching" states of Ne_3 within the first three channels.

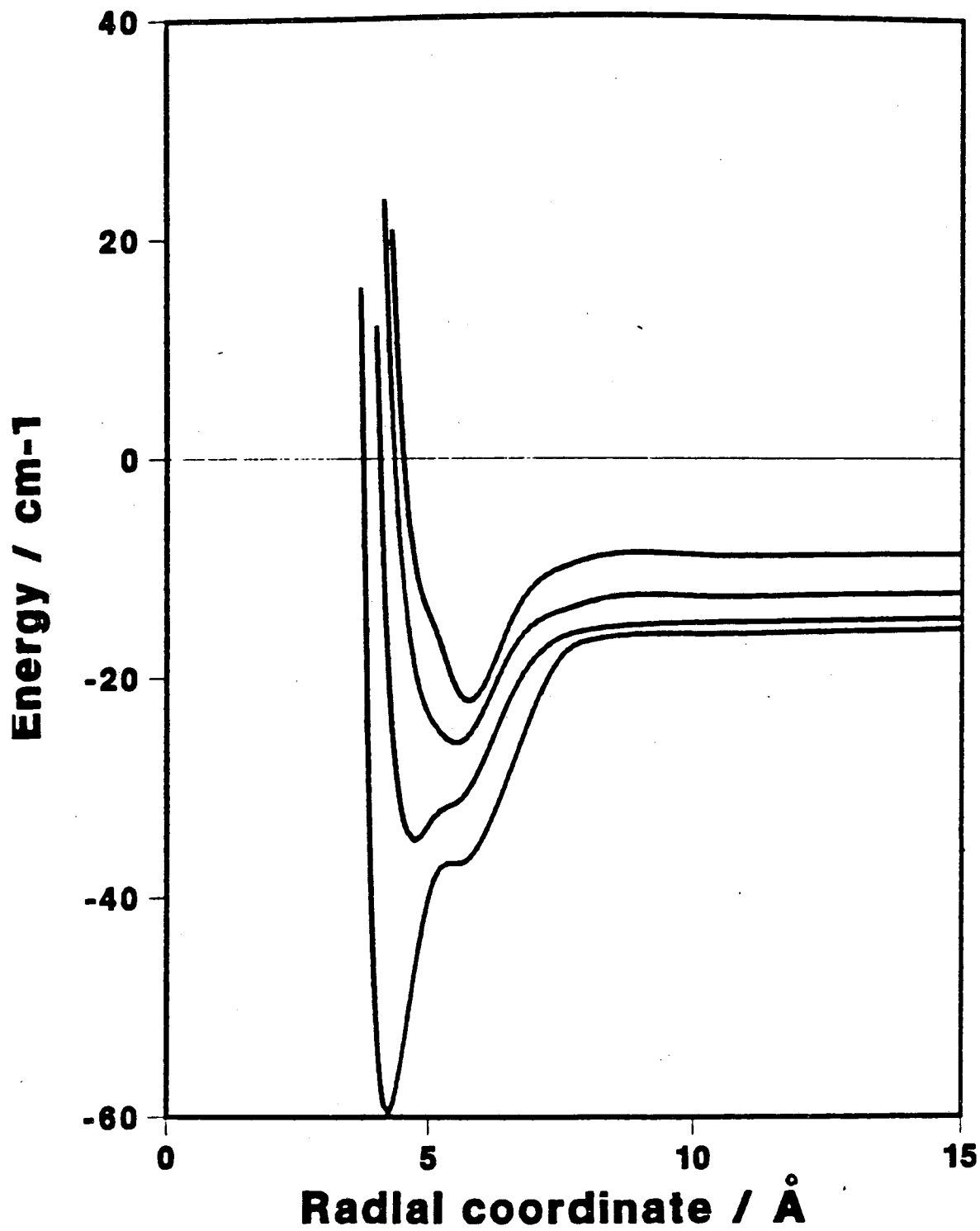


Table 1

J	$E_{\text{Ne}_2}/\text{cm}^{-1}$	$E_{\text{asym}}/\text{cm}^{-1}$
0	-15.53	-15.53
2	-14.59	-14.57
4	-12.41	-12.34
6	-9.03	-8.75

Comparison of the asymptotic limit (E_{asym}) of the adiabatic channel potentials with the vibration-rotation energy levels of Ne_2

Table 2
E/cm⁻¹

n	1	2	3
0	-48.05	-29.91	-22.05
1	-34.29	-23.11	-15.17
2	-28.04	-16.66	-12.35
3	-20.95	-14.70	
4	-15.95		

The "stretching" states of Ne₃ within the first 3 channels.

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