The infrared spectrum of the used catalyst is similar to that of $[\text{Os}_2(\text{CO})_8]^{2-}$ (Table IV), and it is plausible that this may be the predominant structure. This cluster has been shown by NMR spectroscopy to have one bridging carbonyl ligand (the others being terminal); the EXAFS data are not expected to be sufficient to determine such a single bridging carbonyl ligand, but there is an indication in the data that there may be such ligand: the Fourier transforms (Figure 7) show a slight discrepancy around 2.1 Å, just where one would expect an Os–C distance for a bridging carbonyl ligand. (This contribution is considered too small to justify its inclusion in the analysis.)

The formation of $[\text{Os}_2(\text{CO})_8]^{2-}$ on a basic support has been observed before;\(^3\) evidently it is formed from $[\text{Os}_2(\text{CO})_8]$ on highly dehydroxylated (highly basic) MgO. The deprotonation of $[\text{HOs}_2(\text{CO})_8]^{-}$ to give this dianion has also been reported to occur on the basic MgO surface.\(^3\)\(^5\) We suggest that at the high temperature of the catalysis experiment, the same deprotonation could have occurred.

We emphasize that the structural models presented here are likely oversimplified; there is no basis in the data for excluding the presence of mixtures in the zeolites. Nonetheless, the data indicate a remarkable simplicity and uniformity of structure. The catalyst is also distinguished by its stability. Researchers have sought for years to stabilize molecular metal clusters to apply them as catalysts.\(^3\)\(^6\) Evidently the osmium carbonyl clusters in the basic zeolite cages begin to meet the sought-for goal, but a proper stabilizing atmosphere (in this case CO or CO + H\(_2\)) is required.

These results, like those of Herron et al.,\(^3\) provide evidence of a relatively new kind of shape-selective catalysis. The better-known examples include reactant shape selectivity (whereby some reactants enter the zeolite cages, whereas other potential reactants are too large and are sieved out); product shape selectivity (whereby some products are too large to leave the cages where they are formed and are therefore converted instead into other products or back into reactants); and transition-state shape selectivity (whereby some products are excluded because the transition states are too large to form in the cages). The new kind of shape selectivity is catalyst shape selectivity, whereby the catalyst is stabilized in the zeolite cages where it is formed because it is too large to migrate out and change structure, such as by sintering.

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Registry No. CO, 630-08-0; $\text{H}_2\text{Os}(\text{CO})_8$, 22372-70-9.

Theoretically Generated Vibration−Rotation−Inversion Spectrum of $\text{Ar−NH}_3$

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Starting from an ab initio potential surface we have calculated the van der Waals vibration−rotation−inversion states of the $\text{NH}_3$−Ar complex. Especially, the $v_{10}(R)$ and $v_{32}(R)$ terms in the anisotropic expansion of the potential appear to be important and it is found that optimization of a single scaling parameter in the latter term yields good agreement between the computed and the recently measured far-infrared and microwave frequencies of ortho and para $\text{NH}_3$−Ar. We have computed all the rovibrational levels up to $J = 15$ and the $\text{NH}_3$ inversion doubling of these levels. A complete theoretical far-infrared spectrum was generated by calculating the intensities of all the allowed transitions from a dipole function. The properties of the ground and excited van der Waals states and the spectra of ortho and para $\text{NH}_3$−Ar agree well with the data available from molecular beam spectroscopy.

1. Introduction

In a set of two earlier papers,\(^1\)\(^2\) we described the ab initio computation of an intermolecular potential surface for the $\text{Ar−NH}_3$ complex and the calculation of the van der Waals vibrational and rotational states of this complex from that surface. At the time of this calculation only one internal rotor (far-infrared) transition was reported and a few overall rotational (microwave) transitions for $J = 0, 1, 2$, and 3 were measured and identified. All these experimental data pertained to the ortho $\text{NH}_3$−Ar species only. The calculated transition frequencies and rotational constants were found to be in rather good agreement with the measurements.

In the meantime, a few more van der Waals vibration/rotation transitions in ortho $\text{NH}_3$−Ar$^{5,6}$ and also some far-infrared and microwave transitions in para $\text{NH}_3$−Ar$^7$ have been observed, which inspired us to study this complex in much more detail. To this end we have extended the calculation of all the low-lying van der Waals states to rotational quantum numbers up to $J = 15$ and we have included the inversion-tunneling of the $\text{NH}_3$ monomer by means of a simple model. Using a dipole function which includes the permanent NH$^+$ dipole as well as the dipole induced on Ar, we have also calculated the intensities of all allowed transitions. Thus, we have generated the complete far-infrared and microwave spectrum as a function of the molecular beam.  

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1. Introduction

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TABLE I: Transformation Properties of the Coordinates (See Appendix)

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Vibration-Rotation-Inversion Spectrum of Ar–NH$_3$


2. Theory

A. Vibration-Rotation-Inversion States. The coordinates used in the present paper are the same as defined in ref 2. Briefly, $R$ is the length of the vector $\mathbf{R}$ that points from the NH$_3$ center of mass to the Ar nucleus (i.e., the dimer bond axis), $\theta$ is the angle between the $C_3$ axis of NH$_3$ and the vector $\mathbf{R}$, and $\phi$ describes the rotation of NH$_3$ about its $C_3$ axis. The angles $\alpha$, $\beta$, and $\gamma$ are the overall rotation angles of the dimer: $\beta$ and $\alpha$ are the polar angles of the vector $\mathbf{R}$ with respect to a space-fixed frame and $\gamma$ describes the rotation of the dimer about $\mathbf{R}$. In addition, we need the coordinate $p$, which is the NH$_3$ inversion coordinate as defined in the Appendix. The vibration-rotation-inversion Hamiltonian can be written as

$$\hat{H} = \hat{H}_{int} + \hat{H}_{vdw}$$

where

$$\hat{H}_{int}(p) = \hat{T}(p) + V_{int}(p)$$

and

$$\hat{H}_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha,\rho) = \sum A_k(j)j^2 + \frac{1}{2\mu R^2} [J^2 + J^2 - 2JJ] - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial \rho^2} + V_{int}(R,\theta,\phi,\gamma,\beta,\alpha)$$

$\hat{H}_{int}$ is the inversion Hamiltonian of the NH$_3$ monomer which depends only on the internal coordinate $\rho$. The expression for the kinetic energy $\hat{T}(p)$ is given by Papousek and Aliev; the potential $V_{int}(p)$ is the well-known double-well potential of NH$_3$ with an inversion barrier of about 2000 cm$^{-1}$. The Hamiltonian $\hat{H}_{vdw}$ describes the van der Waals vibrations, internal rotations, and overall rotations of the Ar–NH$_3$ complex. It has essentially the same form as given in ref 2. Only the dependence of the rotational constants $A_k$ on $\lambda = x, y, z$ of NH$_3$ and of the intermolecular potential $V_{int}$ on the inversion coordinate $\rho$ is now explicitly expressed. The operator $J$ is the angular momentum of the NH$_3$ monomer with respect to the embedded dimer frame and $\hat{J}$ is the overall angular momentum of the dimer. Exact quantum numbers are $J$ and $M$, i.e., the total angular momentum and its space-fixed $z$ component. An approximate quantum number is the helicity $\omega$ which is the component of both $J$ and $\hat{J}$ along the vector $\mathbf{R}$. The only terms in $\hat{H}_{vdw}$ that couple functions with different $\omega$ are the small off-diagonal Coriolis interactions contained in the operator $(3j/2aR)^2$.

The molecular symmetry group of the inverting NH$_3$-Ar complex described by the Hamiltonian (1) is the permutation-inversion group $\text{P}(D_{3h})$ (see Tables I and II and the Appendix). The ortho states with $A_g'$ and $A_g''$ symmetry combine with the proton spin quartet and have spin statistical weight 12, since the nitrogen nucleus has spin $I = 1$. The para states with $E'$ and $E''$ symmetry combine with the proton spin doublet and have weight 6 and the $A_u'$ and $A_u''$ states are Pauli forbidden. Since the dipole moment function (see section 2B) is of symmetry $A_g''$, the allowed infrared and microwave transitions are $A_g'$, $A_u'$, $E'$ and $E''$. In ref 2 we have described calculation of the eigenstates of $\hat{H}_{vdw}$ for fixed $\rho = \rho_0$, i.e., for a rigid NH$_3$ monomer. We denote these eigenstates as $|\psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha)\rangle$. In order to understand this model one should realize that the motion along the $\rho$ coordinate involves two processes with vastly different time scales. The first process is the $v_2$ umbrella vibration with fundamental frequency 950 cm$^{-1}$. This vibration is an oscillation in one of the two wells in $V_{vdw}(p)$ with ground-state wave function $\psi_0(p)$. Since this vibration is much faster than the van der Waals motions of the Ar–NH$_3$ dimer it is justified to average $\hat{A}_m(p)$ and $V_{int}$ in eq 3 over the function $\psi_0(p)$. And, since $\psi_0(p)$ is rather localized around this equilibrium value $\rho = \rho_0$, the calculation of the van der Waals states may also be performed for fixed $\rho = \rho_0$ (as we have actually done).

The second type of motion in the coordinate $\rho$ is the inversion-tunneling of NH$_3$. In the free NH$_3$ molecule this tunneling between the two wells in $V_{vdw}(p)$ is taken into account by the wave functions

$$\psi_0(p) = \frac{1}{\sqrt{2}} (\psi_{\rho} + \psi_{\rho})$$

where $\hat{E}$ is the identity and $\hat{E}^*$ represents inversion of the system. The energies that correspond with these wave functions are $E_0 = \pm \Delta$, where

$$E_0 = \langle \psi_0(p) | \hat{H}_{int}(p) | \psi_0(p) \rangle$$

is the zero-point energy of the $v_2$ vibration and

$$\Delta = \langle \psi_0(p) | \hat{H}_{vdw}(p) | \psi_0(p) \rangle$$

is the tunneling matrix element. The tunneling frequency in free NH$_3$ is $2|\Delta| = 0.8$ cm$^{-1}$. This tunneling frequency is considerably lower than the frequencies of the van der Waals vibrations and internal rotations in Ar–NH$_3$ which are typically $\sim 20$ cm$^{-1}$. Therefore, we may start with the "localized" wave functions $|\psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha)\rangle$ which are adapted to the symmetry group $\text{P}(C_3h)$. Subsequently, the inversion-tunneling in the Ar–NH$_3$ complex is included by the adaptation of these wave functions to $\text{P}(D_{3h})$, which is the symmetry group of the inverting complex (see the Appendix). The resulting vibration-rotation-inversion wave functions are

$$\Psi_{\pm} = \frac{1}{\sqrt{2}} (\psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) \pm \hat{E}^* \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha))$$

and the corresponding energies are

$$E_{\pm} = \langle \Psi_{\pm} | \hat{H}_{int} + \hat{H}_{vdw} | \Psi_{\pm} \rangle$$

= $E_0 \pm \langle \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) | \hat{E}^* \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) \rangle \Delta$

= $E_0 + \langle \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) | \hat{H}_{int} | \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) \rangle + \langle \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) | \hat{H}_{vdw} | \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) \rangle \pm \langle \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) | \hat{E}^* \psi_{vdw}(R,\theta,\phi,\gamma,\beta,\alpha) \rangle$.

In writing the first two terms we have used that $\hat{H}_{int}$ depends only on the monomer coordinate $\rho$ and we have substituted eqs 7, 5, and 6. The third term in eq 8 is the energy of the van der Waals vibrations and rotations of the Ar–NH$_3$ complex $\hat{H}_{vdw}$, which we have calculated with the assumption that $\psi_0(p)$ is localized at $\rho = \rho_0$ (as discussed above). The fourth term can be neglected with respect to the second term, because the overlap distribution $\langle \psi_{vdw} | \psi_{vdw} \rangle$ is very small and the monomer Hamiltonian $\hat{H}_{int}$ which occurs in $\Delta$, is much larger than $\hat{H}_{vdw}$. For instance, the potential $V_{vdw}(p=0)$ is about 2000 cm$^{-1}$ relative to $V_{vdw}(\rho_0)$, while the cor-
responding difference in $V_{int}$ is only of the order of 20 cm$^{-1}$ (see ref 1).

In ref 2 we have described the calculation of the wave functions

$$\Psi_{\text{CH}}(R, \theta, \phi, \alpha, \beta, \gamma) = \sum_{\tilde{j} \tilde{k} \tilde{l} \tilde{m}} \tilde{c}_{\tilde{j} \tilde{k} \tilde{l} \tilde{m}} \Psi_{\tilde{j} \tilde{k} \tilde{l} \tilde{m}}(R)$$

(9)

in terms of the basis

$$|j k \Omega \Omega_{\text{NMn}}\rangle = \left[\frac{(2j + 1)(2j + 1)}{32\pi}\right]^{1/2} D_{\tilde{l}\tilde{m}}^{j}(\Omega, \theta, \phi) \ast D_{\tilde{j}\tilde{k}}^{j}(\alpha, \beta, \gamma) \ast R^{\tilde{j}} \chi_{\tilde{l}}(R)$$

(10)

which consists of Wigner rotation functions$^9$ and radial basis functions $R^{\tilde{j}} \chi_{\tilde{l}}(R)$.$^{10}$ Operating with $\vec{E}$ on this basis (see Table II) and using its orthonormality, we derive a simple expression for the second term in eq 8. The combination of these results yields, according to our model,

$$E_a = E_0 + E_d^{NM} \pm \sum_{\tilde{j} \tilde{k} \tilde{l} \tilde{m}} \tilde{c}_{\tilde{j} \tilde{k} \tilde{l} \tilde{m}}^* \tilde{c}_{\tilde{j} \tilde{k} \tilde{l} \tilde{m}} |\Delta\rangle$$

(11)

The implication of this expression is that the rovibrational states of $\text{Ar}-\text{NH}_3$ are split by inversion-tunneling. The splittings can be simply calculated from the expansion coefficients of the van der Waals states, eq 9. If these states are free internal rotor states, i.e., if $j$ and $k$ are good quantum numbers so that the summations in eqs 9 and 11 run only over $\Omega$ and $n$, then it can be shown that the splittings obtained from eq 11 are equal to the splittings $2|\Delta|$ in free $\text{NH}_3$. In reality, states with different $j$ and $k$ are mixed by the anisotropic potential $V_{int}$ and the splittings are reduced. If we neglect the (small) Coriolis coupling, then the state in eq 9 is labeled by $\Omega$ and the summation is restricted to this value of $\Omega$. The eigenvectors for the states with positive $\Omega$ have zero components with $\Omega$ and vice versa, so that eq 11 yields a vanishing splitting. The reduction of the inversion-splitting in $\text{Ar}-\text{NH}_3$ is caused by the asymmetry induced in the $\text{NH}_3$ double-well potential by the presence of the Ar atom. In our model this asymmetry is reflected in the coefficients of the wave functions in eq 9. Permutation symmetry is important too: in the ortho species the wave functions must contain an equal weight of $\Omega$ and $-\Omega$ basis functions, whereas in the para dimers these basis functions belong to different sub species. Moreover, we find that in ortho $\text{NH}_3$-Ar only one of the states in eq 7 is Pauli allowed, just as for free $\text{NH}_3$. For the states of $A_1$ symmetry in $\text{Pt}(C_2)$ this is $\Psi_{\text{CH}}$, which is of $A_2''$ symmetry in $\text{Pt}(O_3)$; for the $A_2$ states it is $\Psi_{\text{CH}}$, which is of $A_2'$ symmetry (see the Appendix). So in ortho $\text{NH}_3$-Ar one cannot observe splittings of the states due to inversion-tunneling, but only shifts.

B. Transition Intensities

In order to compute the transition intensities we need an analytic form of the dipole surface. The space-fixed spherical components of the dipole function can be expanded in the same angular basis as the wave functions (cf. eq 10)

$$\mu_m = \sum_{\Lambda \Sigma \Omega} d_{\lambda \mu \omega}^{j}(R, \theta, \phi) \ast D_{\Lambda \Sigma}^{j}(\alpha, \beta, \gamma) \ast (m = 0, \pm 1)$$

(12)

Writing $Q^{(\Lambda)}$ for the spherical components of the $A_2''$-pole on $\text{NH}_3$ expressed in a body-fixed $\text{NH}_3$ frame (the frame $F_{\text{C}}$ of the Appendix) and using the transformations (A5) and (A16), we find for the permanent dipole on $\text{NH}_3$

$$d_{\mu \omega}^{NM}(R) = \delta_{\mu \omega} d_{\mu \omega}^{NM}$$

(13)

The $2\times$-pole on $\text{NH}_3$ yields an electric field $\mathbf{F}(r)$, which expressed in the dimer frame is

$$F_{\text{dimer}}(r) = -\nabla V(r) = -\nabla \sum_{k} \tilde{Q}_{\tilde{k}}(\tilde{r}) \ast \vec{l}_{\tilde{k}} \ast \tilde{C}_{\tilde{k}}(\tilde{r})$$

(14)

where $\tilde{C}_{\tilde{k}}(\tilde{r})$ is a spherical harmonic function in the Racah normalization. The components of the $2\times$-pole in the dimer frame are connected to the body-fixed components by

$$\tilde{Q}_{\tilde{k}}(\tilde{r}) = \sum_{\mu \omega} D_{\mu \omega}^{(\tilde{k})}(\gamma, \theta, \phi) \ast \tilde{Q}_{\mu \omega}^{(\tilde{k})}(\tilde{r})$$

(15)

By the use of the gradient formula$^9$ followed by substitution of $\tilde{C}_{\tilde{k}}(\tilde{r})(0,0) = \delta_{\mu \omega}$, we find that the field $F_{\text{dimer}}$ at the position $(0,0,R)$ of the argon atom is

$$F_{\text{dimer}}(0, 0, R) =$$

$$\delta_{\mu \omega} \sum_{\chi \phi} \left(\begin{array}{c} \lambda' \\lambda \\lambda \\ \mu' \\mu \\mu \end{array}\right) \sum_{\tilde{k}} D_{\mu \omega}^{(\tilde{k})}(\gamma, \theta, \phi) \ast \tilde{Q}_{\mu \omega}^{(\tilde{k})}(\tilde{r})\left(\begin{array}{c} \lambda' \\lambda \\lambda \\ \mu' \\mu \\mu \end{array}\right) \sum_{\tilde{k}} D_{\mu \omega}^{(\tilde{k})}(\gamma, \theta, \phi) \ast \tilde{Q}_{\mu \omega}^{(\tilde{k})}(\tilde{r})\left(\begin{array}{c} \lambda' \\lambda \\lambda \\ \mu' \\mu \\mu \end{array}\right)$$

(16)

The expression in large parentheses is a Wigner 3j symbol.

Rotation from the dimer frame to the space-fixed frame and transfer of $\delta_{\mu \omega}$ from one $D$ matrix to the other yields an expression for the space-fixed components of $\mathbf{F}$ at the position of argon in the required form of eq 12. So, we have for the argon dipole induced by the $2\times$-pole on $\text{NH}_3$

$$d_{\mu \omega}^{NM}(0, 0, R) =$$

$$\sum_{\chi \phi} \left(\begin{array}{c} \lambda' \\lambda \\lambda \\ \mu' \\mu \\mu \end{array}\right) \sum_{\tilde{k}} D_{\mu \omega}^{(\tilde{k})}(\gamma, \theta, \phi) \ast \tilde{Q}_{\mu \omega}^{(\tilde{k})}(\tilde{r})\left(\begin{array}{c} \lambda' \\lambda \\lambda \\ \mu' \\mu \\mu \end{array}\right) \sum_{\tilde{k}} D_{\mu \omega}^{(\tilde{k})}(\gamma, \theta, \phi) \ast \tilde{Q}_{\mu \omega}^{(\tilde{k})}(\tilde{r})\left(\begin{array}{c} \lambda' \\lambda \\lambda \\ \mu' \\mu \\mu \end{array}\right)$$

(17)

where $\alpha^{\text{NM}}$ is the dipole polarizability of $\text{Ar}$.

For randomly oriented dimers which obey a Boltzmann distribution law with temperature $T$ the integrated absorption coefficient for the transition between the spatially degenerate levels labeled by $J_j$ and $J'i'$ is given (in SI units) by

$$\frac{\pi \gamma \lambda \beta}{3h^2 cG Z} \left(\frac{E_{\text{dimer}}(0, 0, R)}{E_d^{NM}} - \frac{E_d^{NM}}{E_d^{NM}}\right) \times \left[ \exp(-E_d^{NM}/kT) - \exp(-E_d^{NM}/kT) \right] S_{jj'}^{Jj'}$$

(18)

where $Z$ is the partition function

$$Z = \sum_{JJ'} g(J + 1) \exp(-E_d^{NM}/kT)$$

(19)

Here $g_c$ is the nuclear spin statistical weight ($g_c = 12$ for all ortho levels, $g_p = 6$ for the para levels) and $N_A$ is Avogadro's number.

If we use eq 12 for the dipole moment $\mu_m$, eqs 9 and 10 for the wave functions $\Psi_{\tilde{j} \tilde{k} \tilde{l} \tilde{m}}$, and the Wigner-Eckart theorem for eliminating the summations over $M$, $M'$ and $m$, we arrive at the following formula for the line strength

$$S_{jj'}^{Jj'} = \sum_{MM'} \sum_{MM'} \mu_m |\mu_m| |J | |M | |J' | |M' | |m |$$

$$\left(\begin{array}{c} \lambda' \\lambda \\lambda \\ \mu' \\mu \\mu \end{array}\right) \left(\begin{array}{c} \lambda' \\lambda \\lambda \\ \mu' \\mu \\mu \end{array}\right)$$

(20)


which is easily evaluated. Applying eqs 18–20 with the corresponding transition frequencies obtained from eq 11 for rotational quantum numbers up to \( J = 15 \), we have generated the complete \( P, Q, \) and \( R \) branches for each van der Waals transition. For the transitions in para \( \text{NH}_3-\text{Ar} \) the calculated absorption coefficients are distributed equally over the two allowed components \( E' \rightarrow E'' \) and \( E'' \rightarrow E' \) which are split by inversion-tunneling.

3. Computational Aspects

In order to perform calculations of the eigenstates in eq 9 which are accurate and yet computationally feasible for rotational quantum numbers as high as \( J = 15 \), we had to follow a procedure which is slightly different from that in ref 2. We use seven radial basis functions \((n_{\text{max}} = 6)\) of the Morse oscillator type\(^{10}\) and angular basis functions up to \( j_{\text{max}} = 9 \) inclusive. In the basis of eq 10 the only terms that connect the blocks with different \( \Omega \) in the Hamiltonian matrix are the small off-diagonal Coriolis interactions. When neglecting these interactions we have to solve a secular problem of dimension \( \leq 700 \) for each value of \( \Omega \) (which is a good quantum number at this level). Next we take all the bound eigenstates plus a number of eigenstates with positive energies (up to about +80 \( \text{cm}^{-1} \)) for ortho \( \text{NH}_3-\text{Ar} \) and about +30 \( \text{cm}^{-1} \) for the para species) from the secular problems with \( \Omega = 0, \pm 1, \) and \( \pm 2 \) and we solve the secular problem in this basis in order to include the off-diagonal Coriolis interactions. These interactions couple blocks with \( \Omega = \pm 1 \) only. This procedure has to be repeated for all values of \( J \leq 15 \) and for the different symmetry species (ortho/para). We have checked that the omission of basis states with \( |\Omega| > 2 \) and energies larger than about +30 \( \text{cm}^{-1} \) does not affect the van der Waals levels presented in this paper to more than 5 \( \times 10^{-5} \text{cm}^{-1} \). The convergence of the rotational energy differences is better by an order of magnitude, as in ref 2. The inversion splittings or shifts of the final eigenstates are calculated from eq 11 and the intensities of all the allowed transitions between these eigenstates from eqs 18–20. In the dipole function (12) we have included the permanent dipole of \( \text{NH}_3 \), eq 13 with \( q_1 (\Omega) = -0.579 \, a_0 q_2 \) and the dipole moment induced on \( \text{Ar} \) (polarizability \( \alpha_\text{p} = 11.06 \, a_0^2 \)) by the dipole and quadrupole of \( \text{NH}_3 \), \( q_3 (\Omega) = -2.45 \, a_0 q_5 \). For the inversion-splitting parameter of free \( \text{NH}_3 \) we have taken the experimental \(^{13} \) value \( \Delta \) = -0.397 \( \text{cm}^{-1} \) which belongs to \( j = 0 \) and \( k = 0 \). The values of \( \Delta \) for the \( \text{NH}_3 \) monomer states with \( j = 1 \) and \( k = 0 \) or \( k = \pm 1 \), which are strongly present in the lowest excited van der Waals states, are not very different (by less than 0.005 \( \text{cm}^{-1} \)).

4. Results and Discussion

A. The Anisotropic Intermolecular Potential.

The ab initio potential for \( \text{Ar}-\text{NH}_3 \), which was calculated in ref 1 (for different values of \( \rho \) and \( \phi \) and used in the computation of the rovibrational states in ref 2 (for \( \rho = \rho_0 \)), was expanded in normalized tesseral harmonics (real spherical harmonics) \( S_{lm} \)

\[
V_{\text{int}}(R, \theta, \phi) = \sum_{lm} (-1)^m v_{lm}(R) S_{lm}(\theta, \phi) \tag{21}
\]

Due to the symmetry of the dimer (see Tables I and II and the Appendix) only terms with \( m = 0, 3, 6, \ldots \) are present in this expansion. In ref 1 it was found that the expansion has converged to about 0.6% accuracy by the inclusion of the 15 terms with \( l \leq 7 \) and \( m \leq 6 \). The parameters which determine the long-range, dispersion and induction, and exponential short-range, exchange \( |\Omega| \) and penetration, contributions to the \( v_{lm}(R) \) are tabulated in ref 1. In Figure 1 we show the dominant terms (for \( \rho = \rho_0 \)). The isotropic potential (\( 4\pi)^{-1/2}v_{00}(R) \) has its minimum at \( R = 3.88 \, \text{Å} \). The largest anisotropic contributions arise from \( v_{10}(R) \) and \( v_{21}(R) \). The latter contribution is the first \( \Phi \)-dependent term in the potential and it gives rise to the global minima at \( \Phi = 0^\circ, 120^\circ, \) and \( 240^\circ \) (see Figure 2 of ref 1, but note that \( \Phi = \pi - \phi \), see eq 1 of ref 1). When ref 2 was written only a few ground-state properties had been determined from microwave spectra\(^4\) and a single internal rotor transition\(^1\) had been measured. Our calculated ground-state rotational constant and expectation values are in fairly good agreement with experiment. The van der Waals “bending” excitation frequency was calculated to be 24.09 \( \text{cm}^{-1} \) (band origin) and found experimentally\(^2\) at 26.47 \( \text{cm}^{-1} \).

Two additional van der Waals excitation frequencies have now been measured\(^5\) for ortho \( \text{NH}_3-\text{Ar} \), as well as the transitions between the three lowest internal rotor states of para \( \text{NH}_3-\text{Ar} \) and the inversion splittings of these states.\(^7\) The levels computed in ref 2 do not agree with these new experimental data. In particular, we notice that the calculated splitting (3.1 \( \text{cm}^{-1} \)) between the two states of ortho \( \text{NH}_3-\text{Ar} \) that correlate with the degenerate \( j = 1, k = 0 \) free internal rotor states is considerably smaller than the observed splitting (10.1 \( \text{cm}^{-1} \)). For the levels that correlate with the \( j = 1, |k| = 1 \) free internal rotor levels in para \( \text{NH}_3-\text{Ar} \), the calculations in ref 2 predict that a state with \( |\Omega| = 1 \) is the ground state of this species, while the experiments show that the \( \Omega = 0 \) level is slightly below this \( |\Omega| = 1 \) level.

In order to establish the origin of these discrepancies we have first calculated the rovibrational levels with the isotropic potential together with each of the anisotropic contributions separately. We found that the effects of the individual anisotropic terms are nearly additive and that the \( v_{10}(R) \) and \( v_{21}(R) \) terms are dominant in determining the splittings between the hindered rotor levels. For the \( v_{21}(R) \) terms this seems somewhat surprising, since the \( j = 1 \) levels of \( \text{NH}_3 \) are not split or shifted by this term in first-order perturbation theory. We observe, however, that the mixing between internal rotor states with different \( j \) values has a substantial (second order) effect on the hindered rotor energies. Next, we have experimented by scaling the \( v_{10}(R) \) and \( v_{21}(R) \) terms. [Actually, we have also tried to scale the \( v_{00}(R) \) term which is used\(^7\) in interpretations of the experimental data. Without excessive scaling this term had very little influence on the van der Waals levels, however.] By scaling \( v_{10}(R) \) with a single parameter, close agreement with the experimental frequencies was obtained. Since the experiments are clearly probing the repulsive region of this term (cf. Figure 1), it was irrelevant whether we scaled the complete \( v_{10}(R) \) term or just the repulsive short-range contribution (although the optimized scaling factors are somewhat different). Multiplication of the short-range parameter \( F_{33} \) (see ref 1) by 1.43

Figure 1. Expansion coefficients (cf. eq 21) of the anisotropic potential from ref 1 (without scaling in \( v_{10} \)).
**Figure 2.** (a, top) Calculated and experimental van der Waals levels (band origins) of ortho NH$_3$-Ar. The leftmost column is obtained from the isotropic potential ($4\pi\rho r^{-1}/\rho_0(R)$); $j$ and $k$ are exact quantum numbers at this level, $v_i$ is the R-stretch quantum number. The second column shows the effect of the $v_1$ term, the third column the cumulative effect of the (scaled) $v_1$ term, and the fourth column the effect of the remaining anisotropic contributions. The quantum number $|Q|$ is approximate. The fifth column includes the inversion-tunneling splittings from eq 11 and the last column contains the experimental frequencies from refs 3, 5, 6, and 7. The dashed levels in the inversion doublets are Pauli forbidden. The arrows indicate calculated and measured transitions, with the ground level adjusted. (b, bottom) Calculated and experimental van der Waals levels of para NH$_3$-Ar. See part a for the explanation. The inversion splitting of the $|Q| = 1$ states is so small that it is not visible on the scale of this figure. The transition between the two inversion-split states of the $\Omega = 0$ level has not been calculated, since we do not expect our inversion-splitting model to yield reliable intensities for this transition.

yields the energy levels displayed in Figure 2, a and b. Specifically, we find that the splitting between the $j = 1, k = 0$ free-rotor states in ortho NH$_3$-Ar is now 10.0 cm$^{-1}$ and that the levels which originate from the $j = 1, |k| = 1$ free-rotor states in para NH$_3$-Ar are ordered correctly with nearly correct splittings. The effects of the various anisotropic terms in the potential on the van der Waals levels are illustrated in Figure 2, a and b, where we consecutively switch on these terms. Finally, we have also calculated the inversion-tunneling splittings of the levels from eq 11. The results of these calculations are shown in Figure 2, a and b, together with the measured excitation frequencies. Keeping in mind that we have optimized only a single parameter, we consider the agreement with experiment to be good and the resulting anisotropic potential to be realistic. In all subsequent calculations we have used this potential.

**B. Calculated Excitation Spectra and Observables: Comparison with Experiment.** For each of the van der Waals vibration/internal-rotation states shown in Figure 2a,b we have calculated the rotational levels up to $J = 15$ inclusive. These levels were fitted by the expression

$$E'' = E^{0i} + B_J(J + 1) - D_J P^2(J + 1)^2 + H_J J^2(J + 1)^3$$

(22)

and the coefficients $E^{0i}$, $B_J$, and $D_J$ in this expression are given in Table III. For the levels with the approximate quantum number $|Q| = 1$ the rotational ladders start at $J = 1$. Paretically, we remark that our quantum number $\Omega$ is sometimes designated by $K$ and that the states with $\Omega = 0$ and $|Q| = 1$ are called $\Sigma$ and $\Pi$ states, respectively. The van der Waals states of the ortho and para species are labeled separately by $i = 0, 1, 2, \ldots$, where $i = 0$ denotes the ground level. The ortho levels 1a and 1b are split by off-diagonal Coriolis interactions, but their origins, i.e., the extrapolated $J = 0$ levels, are the same. As shown in Table IV, the para levels $i = 0, 1, 2$ are split into doublets 0a and 0b, 1a and 1b, 2a and 2b by the inversion-tunneling of NH$_3$. For the $\Omega = 0$ levels 0a and 0b this tunneling splitting is about 90% of the NH$_3$ monomer splitting, but for the levels with $|Q| = 1$ the splitting almost vanishes. If $\Omega$ were a good quantum number this splitting (as calculated from eq 11) would vanish exactly, since the degenerate components of these states (with E symmetry) would correspond with $\Omega = +1$ and with $\Omega = -1$, respectively. The small splittings $=10^{-3}$ cm$^{-1}$ are caused by the admixture of $\Omega = 0$ basis functions into these states, through off-diagonal Coriolis interactions. This explains why the splitting $=10^{-4}$ cm$^{-1}$ between the levels 1a and 1b, which lie very close to the $\Omega = 0$ levels 0a and 0b, is considerably larger than the splitting $=10^{-4}$ cm$^{-1}$ between the levels 2a and 2b which lie much higher. It also explains why the small tunneling splittings of the $|Q| = 1$ states are found to be proportional to $J(J + 1)$, whereas the splitting of the $\Omega = 0$ state is only weakly $J$ dependent. Another consequence of the strong Coriolis mixing between the $\Omega = 0$ levels 0a and 0b and the $|Q| = 1$ levels 1a, 1b is that the individual levels cannot be represented by eq 22. Only the sums of these level energies can be fitted (see Table III), but their differences depend sensitively on the Coriolis coupling.

In Table IV we have listed some radial and angular expectation values calculated for the different van der Waals states. Note that the rotational constants which are calculated as expectation values $B = (\hbar^2/2\mu R^2)$ over the lowest allowed rotational level.
TABLE IV: Energies and Expectation Values of the Dimer Bond Length ($R$), of the Rotational Constant $B = \langle h^2/2\mu R^2 \rangle$, and of the First and Second Legendre Polynomials ($P_1(\cos \vartheta)$) and ($P_2(\cos \vartheta)$) for the Lowest Level in Each Ladder, and the Related Quantities $R_0 = (R^2)^{-1/2}$, $\vartheta_1 = \arccos (P_1(\cos \vartheta))$ and $\vartheta_2 = \arccos ([1/2(P_2(\cos \vartheta)) + 1])^{1/2}$

<table>
<thead>
<tr>
<th>vDW state $i$</th>
<th>lowest $J$ value</th>
<th>energy, cm$^{-1}$</th>
<th>$(R)$, Å</th>
<th>$B$, GHz $(R_0)$, Å</th>
<th>$(P_1(\cos \vartheta))$ $(\vartheta_1)$, deg</th>
<th>$(P_2(\cos \vartheta))$ $(\vartheta_2)$, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>$J = 0$</td>
<td>$-87.943$</td>
<td>3.786</td>
<td>2.983</td>
<td>0.325</td>
<td>-0.052</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($+0.303$)</td>
<td>(3.767)</td>
<td>(71.0)</td>
<td>(56.9)</td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>$J = 1$</td>
<td>$-70.543$</td>
<td>3.745</td>
<td>3.048</td>
<td>0.186</td>
<td>-0.232</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($-0.347$)</td>
<td>(3.726)</td>
<td>(79.3)</td>
<td>(65.0)</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>$J = 1$</td>
<td>$-70.540$</td>
<td>3.745</td>
<td>3.048</td>
<td>0.186</td>
<td>-0.232</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($-0.347$)</td>
<td>(3.726)</td>
<td>(79.3)</td>
<td>(65.0)</td>
<td></td>
</tr>
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<td>2</td>
<td>$J = 0$</td>
<td>$-61.419$</td>
<td>3.948</td>
<td>2.743</td>
<td>0.044</td>
<td>-0.037</td>
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<tr>
<td></td>
<td></td>
<td>($+0.312$)</td>
<td>(3.928)</td>
<td>(87.5)</td>
<td>(56.2)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$J = 0$</td>
<td>$-56.052$</td>
<td>3.921</td>
<td>2.787</td>
<td>0.079</td>
<td>0.290</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($-0.258$)</td>
<td>(3.897)</td>
<td>(85.5)</td>
<td>(43.5)</td>
<td></td>
</tr>
<tr>
<td>para</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0a/0b</td>
<td>$J = 0$</td>
<td>$-77.796$</td>
<td>3.717</td>
<td>3.092</td>
<td>0.174</td>
<td>-0.250</td>
</tr>
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<td></td>
<td></td>
<td>($\pm0.350$)</td>
<td>(3.700)</td>
<td>(80.0)</td>
<td>(65.9)</td>
<td></td>
</tr>
<tr>
<td>1a/1b</td>
<td>$J = 1$</td>
<td>$-76.605$</td>
<td>3.767</td>
<td>3.012</td>
<td>0.425</td>
<td>-0.009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($\pm0.004$)</td>
<td>(3.749)</td>
<td>(64.8)</td>
<td>(55.1)</td>
<td></td>
</tr>
<tr>
<td>2a/2b</td>
<td>$J = 1$</td>
<td>$-67.561$</td>
<td>3.739</td>
<td>3.060</td>
<td>0.048</td>
<td>-0.217</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($\pm0.000$)</td>
<td>(3.719)</td>
<td>(87.2)</td>
<td>(64.3)</td>
<td></td>
</tr>
</tbody>
</table>

*Coriolis interactions included; the additional tunneling shifts from eq 11 is given in parentheses. *Experiment: 4 the value $(P_1(\cos \vartheta)) = 0.17$ ($\vartheta_1 = 80.2^\circ$) is obtained by correction of the experimental value of 0.191 for the induced dipole moment given by eq 17. *Experiment: 5, 6, 7 $(P_2(\cos \vartheta)) = -0.086$ ($\vartheta_2 = 58.3^\circ$). *Experiment: 3, 4, 5, 7 $(P_2(\cos \vartheta)) = -0.221$ ($\vartheta_2 = 64.5^\circ$). *Experiment: 3, 5, 7 $(P_1(\cos \vartheta)) = 0.069$ ($\vartheta_1 = 52.0^\circ$). *Experiment: 7, 8, 9, 10, 11, 12 $(P_1(\cos \vartheta)) = 0.389$; 9, 10, 11, 12 $(P_2(\cos \vartheta)) = 0.007$; 9, 10, 11, 12 $(P_2(\cos \vartheta)) = 0.008$, for $i = 1, 0, 1$, and 2, respectively.

Figure 3. Rotational branches of the lowest ($i = 0 \rightarrow 1$) van der Waals (internal rotor) $|\Omega| = 0 \rightarrow 1$ transition in ortho NH$_3$-Ar as calculated for $T = 5$ K (intensity in $10^{10}$ m$^2$ s$^{-1}$ mol$^{-1}$).

Figure 4. Rotational branches of the ($i = 0 \rightarrow 2$) van der Waals (internal rotor) $|\Omega| = 0 \rightarrow 1$ transition in para NH$_3$-Ar as calculated for $T = 5$ K (intensity in $10^{10}$ m$^2$ s$^{-1}$ mol$^{-1}$). The two windows contain the spectra for the allowed ($E' \leftrightarrow E''$) transitions between inversion doublets (see Table V).

(i.e., $J = 0$ or $J = 1$) of each state are different from the values of $B$ in Table III which were obtained from the fit of all rotational levels with $J \leq 15$ by eq 22. This difference is caused by the Coriolis shifts of the rotational levels, as explained in ref 5. These Coriolis shifts explain, in particular, why the levels 1a and 1b of ortho NH$_3$-Ar have different effective $B$ values (see Table III) although the expectation values $B$ in Table IV are the same.

In Figures 3, 4, and 5 and in Table V we have displayed the results of the intensity calculations. A molecular beam temperature of 5 K has been assumed, but it is easy to generate the spectra for any other temperature (although, of course, for high temperatures they would no longer be complete). The intensities for the ortho and para NH$_3$-Ar species have been calculated separately and it has been assumed that these species are present in the ratio 2:1, as determined by their nuclear spin statistical weights. In fact, this ratio will depend on the kinetics of the dimer formation, which occurs somewhere between room temperature and 5 K. The binding energy with respect to the monomer ground states, which is slightly larger for the para than for the ortho complex, might play a role in this formation. It follows from Table...
TABLE V: Transition Frequencies and Intensities

<table>
<thead>
<tr>
<th>transition</th>
<th>band origin, cm$^{-1}$</th>
<th>P(2)</th>
<th>Q(2)</th>
<th>R(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 → 1a</td>
<td>16.545 (16.415)$^a$</td>
<td>77.59 (85.09)</td>
<td>412.33 (450.35)</td>
<td>359.54 (390.38)</td>
</tr>
<tr>
<td>0 → 1b</td>
<td>26.533 (26.471)$^b$</td>
<td>14.12 (12.82)</td>
<td>18.40 (16.30)</td>
<td>252.54 (211.78)</td>
</tr>
<tr>
<td>0 → 2</td>
<td>31.329 (34.318)$^b$</td>
<td>186.09 (158.83)</td>
<td>10.87 (10.21)</td>
<td>0.42 (0.48)</td>
</tr>
<tr>
<td>0 → 3</td>
<td>3.01 (3.26)</td>
<td>0.09 (0.10)</td>
<td>77.59 (85.09)</td>
<td>13.27 (14.37)</td>
</tr>
</tbody>
</table>

$^a$In parentheses: the intensity contribution from the permanent dipole. The HönL-London factors$^{16}$ for these transitions are P(2):Q(2):R(2) = 2:0:3 for $\Omega = 0 → 0$; 1.5:4 for $[\Omega] = 0 → 1$; 9.5:16 for $[\Omega] = 1 → 1$.

V that the absorption intensities are dominated by the permanent dipole on NH$_3$. The contributions from the dipole moments are simple. They contain P and R branches of nearly equal intensities and no Q branches, and they look like the parallel ft = 0 → 0 bands in normal rigid-rotor spectra. The floppiness of the complex is reflected by a rather large increase of the rotational constant upon excitation and by the relatively large distortion constants. In the spectra of Figures 3, 4, and 5 the intensities of the R branches are larger than the intensities of the P branches. For perpendicular (|$\Omega$| = 0 → 1) bands this intensity ratio is normal; it follows from the HönL-London factors$^{16}$ (see Table V). These factors arise directly from eq 20 if one keeps in mind that $\Omega$ is a nearly good quantum number. For the |$\Omega$| = 1 → 1 transitions in the para species the calculated P:Q:R intensity ratio does not correspond with the HönL-London factors, however. It is closer to the ratio expected for |$\Omega$| = 0 → 1 transitions. This must be due to the Coriolis mixing between the $\Omega = 0$ states 0a, 0b and the |$\Omega$| = 1 states 1a, 1b, which causes the weak |$\Omega$| = 1 → 1 transitions to pick up intensity from the much stronger |$\Omega$| = 0 → 1 transitions.

Finally we compare our results with the experimental data which are also given in Tables III, IV, and V. The van der Waals excitation frequencies agree to within about 10% on the average, the rotational constants B deviate by about 3%, i.e., the average distance $R_R$ by about 1.5%, and the calculated distortion constants D deviate by about 40%. These results may be checked against the relation between the rotational constant B, the distortion constant D, and the stretch frequency $\nu_s$:

$$D = 4B^3/\nu_s^2$$

which has been derived for diatomics.$^{4,17}$ Both the calculated and the experimental values and also the deviations between calculations and experiment are consistent with this relation. Since the calculations of the rovibrational states are very accurate, we conclude that all these discrepancies result from the potential surface, which is thus amenable to further improvement.

We emphasize, however, that the present calculations are not intended to produce results of spectroscopic accuracy. They are meant to yield a realistic picture of the motions in this complex, to help with the interpretation of the spectra, and to understand the features observed in these spectra. In this respect they are quite successful. The nearly free internal rotor character of the van der Waals states is clearly exhibited (see also ref 2) and the angular expectation values (see Table IV) are realistic. The calculated changes in the rotational constant $B$ and in the angular expectation value ($P_2(\cos \theta)$) from one van der Waals state to another agree well with experiment in general. As found already in ref 2, the bending excitation in ortho NH$_3$-Ar is strongly mixed with the stretch excitation. It seems from the expectations values (R), B, and ($P_2(\cos \theta)$) and from the signs of the tunneling shifts in Table IV that the lower (i = 2) state had dominant stretch excitation character, while the higher (i = 3) state involves more dominantly the bending (internal rotor) excitation. This is contrary to the result found in ref 2 and it is not confirmed by the experimental data. It must be caused by the remaining imperfections in the anisotropic potential.

The inversion doubling of the rovibrational states in para NH$_3$-Ar and the near quenching of this doubling in the |$\Omega$| = 1 states agree well with the spectroscopic data (see Table IV) and can now be understood. We find that the intensities for the different van der Waals bands are different by 3 orders of magnitude (see Table V). The intensity ratios between the R(3) transitions in several bands have recently been observed.$^7$ It is found experimentally that the ratio of $P_0 = 0 → 1$ transitions from the ground state (i = 0) to the 1a, 1b states in ortho dimers is about 30 times stronger than the |$\Omega$| = 0 → 1 transitions from the 0a, 0b states to the 2a, 2b states in para dimers. The calculated intensity factor between these transitions is about 25 (cf. Figures 3 and 4). The latter transition is observed$^7$ to be about 15 times stronger than the |$\Omega$| = 1 → 1 transition from the 1a, 1b states to the 2a, 2b states in para dimers, while the calculated factor is about 20 (cf. Figures 4 and 5). So the agreement between these experimental intensity ratios and our calculations is very good.

The intensities also yield information on the mixing between the bending and the stretch excitations in ortho dimers. Experimentally it is found that the intensity ratio between the band and Figure 3 the bending transition at 26.5 cm$^{-1}$ is about 2.5. From the present calculations and those in ref 2 we can extract that a pure bending excitation is much stronger than a pure stretch excitation. This is due to the fact that the dominant part of the dipole surface is independent of R, cf. eq 13, but depends on $\Omega$. Taking this into account and comparing the intensities of the ortho transitions in Table V we must conclude that the present calculations overestimate the stretch character of the lower excitation at 16.5 cm$^{-1}$ and the bending character of the higher excitation at 26.5 cm$^{-1}$. This conclusion was already indicated by the expectation values discussed above. Finally, we observe that the intensity ratios between the P, Q, and R branches of the parallel $\Omega = 0 → 0$ and |$\Omega$| = 1 → 1 bands and the perpendicular |$\Omega$| = 0 → 1.

\[ f_j = \sqrt{\frac{1}{6}(2CH_1 - CH_2 - CH_3)} \]
\[ f_y = \sqrt{\frac{1}{2}(CH_2 - CH_3)} \]
\[ f_z = f_x \times f_y \]  \hspace{1cm} (A9)

The vectors \( f_j, f_y, f_z \) span the two-dimensional irrep \( E \) of the permutation group \( S_3 \subset \text{PI}(D_{3h}) \) and \( f_x \) spans the antisymmetric representation \( A_2 \) of this group. For the generators (123) and (23) we have therefore

\[ (123)f_c = \hat{I}_D R_c(-2\pi/3) \]  \hspace{1cm} (A10)
\[ (23)f_c = \hat{I}_D R_c(\pi) \]  \hspace{1cm} (A11)

with \( \hat{I}_D = (f_x f_y f_z) \). In order to consider the effect of \( \hat{E}^* \) on \( \hat{I}_D \), we first observe that this frame is invariant under a change of origin, e.g.

\[ \hat{E}^* f_c = \hat{I}_D \]  \hspace{1cm} (A12)

The frame \( \hat{I}_D \) is not necessarily orthonormal. In the case of an ammonia molecule with \( C_3v \) point group symmetry, which we obtain by imposing the constraints

\[ \overline{CH_1 CH_2} = h^2 \cos \omega(i-j), \quad i, j = 1, 2, 3 \]  \hspace{1cm} (A13)

the frame is orthogonal, however, and the basis vectors can be normalized. The normalization factors of \( f_x, f_y, f_z \) are equal, so that the permutation properties of the frame are not affected by normalization. From here on we assume that \( NH_3 \) has \( C_3v \) point group symmetry, i.e. \( f_z \) is the 3-fold axis, and that the frame \( \hat{I}_D \) is orthonormal.

We define the \( NH_3 \) inversion coordinate \( \rho \) as the inner product of two collinear vectors

\[ \rho = \overline{CN} f_z \]  \hspace{1cm} (A14)

Since \( \overline{CN} \) is invariant under permutations of the protons, \( \rho \) inherits its permutational properties from \( f_z \); i.e. \( \rho \) transforms as \( A_2 \) of \( S_3 \). In order to consider the effect of \( \hat{E}^* \), we evaluate the inner product of eq A14 in the space-fixed basis at \( D \)

\[ \overline{CN} = \overline{D N} - \overline{D C} = \overline{D}(N-C) \]  \hspace{1cm} (A15)

and, since \( \overline{D} \) is invariant under translation as well as under inversion (cf. eq A12), we find \( \hat{E}^* \rho = \rho \). The Euler angles of \( NH_3 \) with respect to the dimer frame are defined by the relation

\[ \hat{I}_D = \overline{\hat{E}}^* \rho = \overline{\hat{E}}^* f_c R_c(\theta) R_c(\phi) \]  \hspace{1cm} (A16)

which is possible due to the fact that both frames are orthonormal and right-handed. From eq A16 follows

\[ \hat{I}_D = \overline{\hat{E}}^* f_c R_c(\theta) R_c(\phi) \]  \hspace{1cm} (A17)

so that the Euler angles \( \theta \) and \( \gamma \) are the polar angles of the symmetry axis \( f_z \) with respect to the dimer frame.

In order to determine the behavior of the Euler angles under the molecular symmetry group, we consider first (using eqs A12, A16, and A6)

\[ \overline{\hat{I}}_D R_c(\pi) = \overline{\hat{E}}^* \hat{I}_D \]
\[ \overline{\hat{I}}_D R_c(\pi) = \overline{\hat{E}}^* \hat{I}_D \]  \hspace{1cm} (A18)

where \( \gamma', \theta', \) and \( \phi' \) are the transformed Euler angles. From eq
Resonances In Valence Shell Photoionizations of Cyanogen. Photoelectron Angular Distribution Parameters of the $\tilde{\Pi}^+_g$, $\tilde{\Sigma}^+_g$, $\tilde{\Sigma}^+_u$, and $\tilde{\Sigma}^+_u$ Ionizations up to a Photon Energy of 28.5 eV

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Photoelectron angular distribution parameters for the first four valence shell photoionizations of cyanogen, for the first one also vibrationally resolved, have been measured by using synchrotron radiation. Compared to earlier measurements, the present ones refer to an extended energy range (14.3–28.5 eV) and are more accurate and precise. Resonance features are noted finally that there is freedom in representing the effect of the symmetries on the Euler angles. For instance, (23) may alternatively be given as (cf. eqs A22, A7, and A8),

$$R_1(\gamma) R_2(\pi-\varphi) R_3(\varphi) = R_1(\gamma) R_2(\pi) R_3(\varphi)$$

whence

$$\gamma' \rightarrow \gamma$$
$$\varphi' \rightarrow \varphi$$

The effect of the other generator (123) on the Euler angles follows from eq A10, and the effect of the other symmetry operations by group multiplication. The results are summarized in Table I.

Introduction

High-resolution angle-resolved photoelectron spectroscopy coupled with a variable-energy photon source allows detailed studies to be made on the photoelectron dynamics of molecules incorporating such phenomena as shape resonances and autoionization processes.1–3 Both types of phenomena give rise to distinct features in molecular photoionization such as rapid variations in photoelectron angular distributions, enhancements in cross sections, and non-Franck–Condon effects in vibrationally resolved spectra.1,2 Precise measurements of the photoelectron angular distribution parameters for ionizations of molecules as a function of the photon energy provide a sensitive probe for the identification of shape resonances and autoionizations. Detailed comparisons of experimental and theoretical results are valuable in characterizing the nature of these phenomena.

Several studies on the photoionization of cyanogen (ethane-dinitrile, N≡C–C≡N), both experimental4–6 and theoretical7–9 have been made before. Based on partial photoionization cross section and photoelectron angular distribution parameter calculations