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The infrared spectrum of the used catalyst is similar to that of \([\text{Os}_6(\text{CO})_{11}]^{2-}\) (Table IV), and it is plausible that this may be the predominant structure. This cluster has been shown by NMR spectroscopy\(^2\) 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 \([\text{Os}_6(\text{CO})_{11}]^{2-}\) on a basic support has been observed before;\(^3\) evidently it is formed from \([\text{Os}_6(\text{CO})_{12}]^{3-}\) on highly dehydroxylated (highly basic) MgO. The deprotonation of \([\text{HOs}_6(\text{CO})_{11}]^{-}\) to give this dianion has also been reported to occur on the basic MgO surface.\(^3\) 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.\(^3\) Evidently the osmium carbonyl clusters in the basic

found to be in rather good agreement with the measurements.

In the meantime, a few more van der Waals vibration/internal-rotation transitions in ortho \(\text{NH}_3-\text{Ar}\)\(^5,6\) and also some far-irrenered and microwave transitions in para \(\text{NH}_3-\text{Ar}\)\(^7\) 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 \(\text{NH}_3\) 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 mo-
The ortho states with \( A_2^\prime \) and \( A_2^\prime\prime \) symmetry combine with the proton spin doublet and have weight 6 and the \( A_1^\prime \) and \( A_1^\prime\prime \) states are Pauli forbidden. Since the dipole moment function (see section 2B) is of symmetry \( A_1^\prime\prime \), the allowed infrared and microwave transitions are \( A_1^\prime \leftrightarrow A_1^\prime\prime \) and \( E \leftrightarrow E \).

In ref 2 we have described calculation of the eigenstates of \( \tilde{H}_{vdW} \) for fixed \( \rho = \rho_0 \), i.e., for a rigid NH3 monomer. We denote these eigenstates as \( \psi^{\text{vdW}}_{\text{in}}(R, \phi, \psi, \beta, \alpha) \). In order to understand this model one should realize that the motion along \( \rho \) coordinate involves two processes with vastly different time scales. The first process is the \( \psi_2 \) umbrella vibration with fundamental frequency 950 cm\(^{-1}\). This vibration is an oscillation in one of the two wells of \( V_{\text{in}}(\rho) \) with ground-state wave function \( f_0(\rho) \). Since this vibration is much faster than the van der Waals motions of the Ar–NH3 dimer it is justified to average \( A_1(\rho) \) and \( V_{\text{in}} \) in eq 3 over the function \( f_0(\rho) \). And, since \( f_0(\rho) \) is rather localized around the 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 NH3. In the free NH3 molecule this tunneling between the two wells in \( V_{\text{in}}(\rho) \) is taken into account by the wave functions

\[
f_\rho(\rho) = \frac{1}{2^{1/2}}(\tilde{E} \pm \hat{E}^\ast) f_0(\rho) = \frac{1}{2^{1/2}}[f_0(\rho) \pm f_0(-\rho)]
\]

where \( \tilde{E} \) is the identity and \( \hat{E}^\ast \) represents inversion of the system. The energies that correspond with these wave functions are \( E_0 \leq \Delta \), where

\[
E_0 = \langle f_0(\rho)|\tilde{H}_{\text{in}}(\rho)|f_0(\rho)\rangle
\]

is the zero-point energy of the \( \psi_2 \) vibration and

\[
\Delta = \langle f_0(\rho)|\hat{H}_{\text{in}}(\rho)|f_0(\rho)\rangle
\]

is the tunneling matrix element. The tunneling frequency in free NH3 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–NH3, which are typically \( \approx 20 \) cm\(^{-1}\). Therefore, we may start with the "localized" wave functions \( \psi^{\text{vdW}}_{\text{in}}(R, \phi, \psi, \beta, \alpha) f_0(\rho) \), which are adapted to the symmetry group \( \text{PI}(C_3) \). Subsequently, the inversion-tunneling in the Ar–NH3 complex is included by the adaptation of these wave functions to \( P(\text{D})_3 \), which is the symmetry group of the inverting complex (see the Appendix). The resulting vibration–rotation–inversion wave functions are

\[
\Psi = \frac{1}{2^{1/2}}(\Psi^{\text{vdW}}(R, \phi, \psi, \beta, \alpha) f_0(\rho)) \pm \hat{E}^\ast(\Psi^{\text{vdW}}(R, \phi, \psi, \beta, \alpha) f_0(\rho))
\]

and the corresponding energies are

\[
E_\pm = \langle \Psi_\pm|\tilde{H}_{\text{in}} + \hat{H}_{\text{vdW}}|\Psi_\pm\rangle
\]

where

\[
E_\pm = \langle \Psi_\pm|\tilde{H}_{\text{in}} + \hat{H}_{\text{vdW}}|\Psi_\pm\rangle \pm \hat{E}^\ast \langle \Psi^{\text{vdW}}(R, \phi, \psi, \beta, \alpha) f_0(\rho)|\hat{H}_{\text{vdW}}|\Psi^{\text{vdW}}(R, \phi, \psi, \beta, \alpha) f_0(\rho)\rangle
\]


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

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<tr>
<th>( P(D_{3h}) )</th>
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<th>( \alpha )</th>
<th>( \gamma )</th>
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<tr>
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<td>( \gamma )</td>
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<td>( \rho )</td>
</tr>
<tr>
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<td>( \beta )</td>
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<td>( \gamma )</td>
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<td>( \varphi )</td>
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</tr>
<tr>
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<td>( \alpha )</td>
<td>( \gamma )</td>
<td>( \theta )</td>
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<td>( \beta )</td>
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<td>( \gamma )</td>
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<td>( \varphi + 2\pi/3 )</td>
<td>( \rho )</td>
</tr>
<tr>
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<td>( \alpha )</td>
<td>( \gamma )</td>
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<td>( \varphi )</td>
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<td>( \rho )</td>
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</table>
responding difference in $V_{\text{int}}$ is only of the order of 20 cm$^{-1}$ (see ref 1).

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

$$\Psi_{\text{CM}}^m(R, \vartheta, \varphi, \gamma, \beta, \alpha) = \sum_{j,k,m} \Psi_{j,k,m}(\alpha, \beta, \gamma) * R^j_x(R)$$

in terms of the basis

$$|j\Omega J M \rangle = \left[ \frac{(2j + 1)(2J + 1)}{32\pi^3} \right]^{1/2} D^{j\Omega}_{00}(0, \vartheta, \varphi) * D^{j\Omega}_0(\alpha, \beta, \gamma) * R^j_x(R)$$

which consists of Wigner rotation functions and radial basis functions $R^j_x(R)$.

Operating with $E^*$ 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,

$$E_a = E_0 + E_{{\text{dip}}'} \pm [(-1)^j \frac{\sum_{k=0}^j (-1)^k \Psi_{j,k,m}(\alpha, \beta, \gamma) \Psi_{j,k,m}(\alpha, \beta, \gamma) \Delta}{\sum_{k=0}^j}]$$

The implication of this expression is that the rovibrational states of Ar$-$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 $\alpha$, then it can be shown that the splittings obtained from eq 11 are equal to the splittings $2|A|$ of the permanent dipole in NH$_3$. In reality, states with different $j$ and $k$ are mixed by the anisotropic potential $V_{\text{int}}$ 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 Ar$-$NH$_3$ is caused by the asymmetry induced in the 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 subspecies. Moreover, we find that in ortho NH$_3$--Ar only one of the states in eq 7 is Pauli allowed, just as for free NH$_3$. For the states of $A_1$ symmetry in $P(C_{3v})$ this is $\Psi_1$ which is of $A_2''$ symmetry in $P(D_{3h})$; for the $A_2$ states it is $\Psi_8$ which is of $A_2'$ symmetry (see the Appendix). So in ortho 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)

$$\mu_m = \sum_{\text{JM}} d_{\text{vuv}}(R) D_{\text{vuv}}^j(0, \vartheta, \varphi) * D_{\text{vuv}}^j(\alpha, \beta, \gamma) * \left( \text{m = 0, } \pm 1 \right)$$

Writing $Q^{(l)}$ for the spherical components of the 2$^\lambda$-pole on NH$_3$ expressed in a body-fixed NH$_3$ frame (the frame $\mathbf{F}$ of the Appendix) and using the transformations ($A_5$) and ($A_16$), we find for the permanent dipole on NH$_3$

$$d_{\text{vuv}}(R) = \delta_1 \delta_0 \delta_0$$

The 2$^\lambda$-pole on NH$_3$ yields an electric field $F(r)$, which expressed in the dimer frame is

$$F_{\text{vuv}}(r) = -\nabla V(r) = -\nabla \sum_k \Psi_k^j(\vartheta, \varphi, \gamma) C_k$$

where $C_k$ is a spherical harmonic function in the Racah normalization. The components of the 2$^\lambda$-pole in the dimer frame are connected to the body-fixed components by

$$\Psi_k^j(\vartheta, \varphi, \gamma) = \sum_{l,m} D_{lj}^j(\vartheta, \varphi, \gamma) C_l^m$$

By the use of the gradient formula followed by substitution of $C_l^m(0,0) = \delta_{lm}$ we find that the field $F_{\text{vuv}}$ at the position (0,0,$R$) of the argon atom is

$$F_{\text{vuv}}(0, 0, R) = -\nabla \sum_k \Psi_k^j(\vartheta, \varphi, \gamma) C_k$$

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

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

$$d_{\text{vuv}}(R) =$$

$$(-1)^j \delta_1 \delta_0 \delta_0$$

where $\delta_1 \delta_0$ is the dipole polarizability of Ar.

For randomly oriented dimers which obey a Boltzmann distribution law with temperature $T$ the integrated absorption coefficient for the transition between the $M$ and $M'$ degenerate levels labeled by $J_i$ and $J'_{ii}$ is given (in SI units) by

$$\int \frac{\pi N \lambda \delta_i}{3 h^2 \lambda^2} \left( E_{\text{dip}}' - E_{\text{dip}}'' \right) \times \left[ \exp(-E_{\text{dip}}'/kT) - \exp(-E_{\text{dip}}''/kT) \right] S_{jj}^f$$

where $Z$ is the partition function

$$Z = \sum_{JJ} g(2J + 1) \exp(-E_{\text{dip}}'/kT)$$

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

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

$$S_{jj}^f = \sum_{\text{MM}''} \left[ \text{m} | \lambda | \mu_m | MJ_i \rangle \mu_m | MJ_i \rangle \right]^2$$

$$\sum_{\lambda \mu \nu} \sum_{\text{JM}''} \sum_{\text{JM}} (-1)^j \left( \frac{2J + 1}{2(J + 1) - 1} \right)^{1/2} C_{\lambda \mu \nu}^j x_{\lambda \mu \nu}^j \left( \frac{R^\lambda_{\text{h}}(R)}{d_{\text{vuv}}(R)} \right) x_{\lambda \mu \nu}^j \left( \frac{R^\lambda_{\text{h}}(R)}{d_{\text{vuv}}(R)} \right) \times \left( \begin{array}{ccc} j' & \lambda & J' \\ J & J' & \lambda \end{array} \right) \left( \begin{array}{ccc} J & J' & \lambda \\ \lambda & J & J' \end{array} \right) \left( \begin{array}{ccc} J' & J & \lambda \\ \lambda & J & J' \end{array} \right) \left( \begin{array}{ccc} J & J' & \lambda \\ \lambda & J & J' \end{array} \right) \right)^2$$


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

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 NH$_3$-Ar the calculated absorption coefficients are distributed equally over the two allowed components $E' ightarrow E''$ and $E'' ightarrow E'$ 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 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 cm$^{-1}$ for ortho NH$_3$-Ar and about +30 cm$^{-1}$ for the para species) from the secular problem 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 $\Delta \Omega = \pm 1$ 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 cm$^{-1}$ does not affect the van der Waals levels presented in this paper to more than 5 $\times$ 10$^{-3}$ cm$^{-1}$. The convergence of the rotational energy differences is better by an order of magnitude, to within 0.1 cm$^{-1}$.

When 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 NH$_3$, eq 13 with $Q(R) = -0.579 \, a_0 \, e^{12}$, and the dipole moment induced on Ar (polarizability $\alpha_{\text{Ar}}^\text{e} = 11.06 \, a_0 \, e^{13}$) by the dipole and quadrupole of NH$_3$, $Q(R) = -2.45 \, a_0 \, e^{14}$. For the inversion-splitting parameter of free NH$_3$ we have taken the experimental value $\Delta = -0.397$ cm$^{-1}$ which belongs to $J = 0$ and $k = 0$. The values of $\Delta$ for the 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 cm$^{-1}$).

4. Results and Discussion

A. The Anisotropic Intermolecular Potential.

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

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

Due to the symmetry of the dimer (see Tables I and II and the Appendix) only terms with $m = 0, 3, 6,...$ 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 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$n^2$)$^{-1/2}v_{00}(R)$ has its minimum at $R = 3.88 \, \text{Å}$. The largest anisotropic contributions arise from $v_{01}(R)$ and $v_{23}(R)$. The latter contribution is the first $\rho$-dependent term in the potential and it gives rise to the global minima at $\rho = 0^\circ$, 120$^\circ$.

![Figure 1. Expansion coefficients (cf. eq 21) of the anisotropic potential from ref 1 (without scaling in $v_{ij}$).](image)

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 and a single internal rotor transition 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 cm$^{-1}$ (band origin) and found experimentally at 26.47 cm$^{-1}$.

Two additional van der Waals excitation frequencies have now been measured for ortho NH$_3$-Ar, as well as the transitions between the three lowest internal rotor states of para NH$_3$-Ar and the inversion splittings of these states. The levels computed in ref 2 do not agree with these new experimental data. In particular, we noticed that the calculated splitting (3.1 cm$^{-1}$) between the two states of ortho NH$_3$-Ar that correlate with the degenerate $j = 1, k = 0$ internal rotor states is considerably smaller than the observed splitting (10.1 cm$^{-1}$). For the levels that correlate with the $j = 1, |k| = 1$ free internal rotor levels in para NH$_3$-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 $v_{00}(R)$ and $v_{23}(R)$ terms are dominant in determining the splittings between the hindered rotor levels. For the $v_{13}(R)$ terms this seems somewhat surprising, since the $j = 1$ levels of 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 $v_{13}(R)$ terms. [Actually, we have also tried to scale the $v_{00}(R)$ term which is used in interpretations of the experimental data. Without excessive scaling this term had very little influence on the van der Waals levels, however. By scaling $v_{00}(R)$ 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 $v_{13}(R)$ 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 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$\pi r^2$ -vdW(R)); $j$ and $k$ are exact quantum numbers at this level, $v_s$ is the R-stretch quantum number. The second column shows the effect of the $v_9 \approx$ term, the third column the cumulative effect of ortho NH$_3$ -Ar. The leftmost column is obtained from this figure. The transition between the two inversion-split states of the |$\ii$| = 1 states is so small that it is not visible on the scale of this figure. The agreement with experiment is good and the resulting anisotropic potential to be realistic. In all subsequent calculations we have used this potential.

Table III: Rotational Level Fit Parameters for the Different van der Waals States (See Eq 22)

| vDW state | [|$\Omega$|] | symmetry | origin $E''$, cm$^{-1}$ | rotational constant $B_r$, GHz | distortion constant $D_p$, KHz |
|-----------|-----------|----------|------------------------|-------------------------------|---------------------|
| ortho     | 0         | even/odd $J$ | $A_s''/A_s''$ | -87.640 | 2.970$^e$ |
|           | 1         |           | $A_s''/A_s''$ | -71.090 | 2.980$^e$ |
|           | 2         |           | $A_s''/A_s''$ | -61.107 | 2.737$^d$ |
|           | 3         |           | $A_s''/A_s''$ | -56.311 | 2.819 |
| para      | 0a        |           | $E'/E''$ | -77.483 | 3.023$^f$ |
|           | 0b        |           | $E'/E''$ | -77.132 | 3.023$^f$ |
|           | 1a        |           | $E'/E''$ | -67.762 | 3.015 |
|           | 1b        |           | $E'/E''$ | -67.762 | 3.016 |

$^e$ Experimental values: $B = 2.8769 (1), D = 86.4 (3), B = 2.876849 (2), D = 88.7 (2), B = 2.8768 (2), D = 88.7 (3).$ $^f$ Experimental values: $B = 2.8019 (2), D = 90.5 (4).$ $^d$ Experimental values: $B = 2.89071 (2), D = 87.1 (3).$ $^d$ Experimental values: $B = 2.8229 (2), D = 102.3 (5).$ $^f$ These states are exact quantum numbers. $^d$ These states lie so close that they are heavily mixed by Coriolis interactions and, thus, cannot be fitted by eq 22 (see text). The quantities given are the arithmetic averages over the two states. $^e$ Experimental values: $B = 2.881046 (5), D = 95.8 (1).$ $^f$ Experimental values: $B = 2.872722 (4), D = 100.5 (1).$

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...
TABLE IV: Energies and Expectation Values of the Dimer Bond Length ($R$), of the Rotational Constant $B = (\hbar^2/2\mu R^2)$, and of the First and Second Legendre Polynomials ($P_1(\cos \theta)$) and ($P_2(\cos \theta)$) for the Lowest Level in Each Ladder, and the Related Quantities $R_0 = (R^{-2})^{-1/2}$, $\theta_1 = \arccos (P_1(\cos \theta))$ and $\theta_2 = \arccos (1/\sqrt{2}(P_2(\cos \theta) + 1))^{1/2}$

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<th>$(B)$, GHz</th>
<th>$(P_1(\cos \theta))$, $^b$ deg</th>
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<td>2.983</td>
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</tr>
<tr>
<td>1a</td>
<td>$J = 1$</td>
<td>$-70.54381 \pm 0.34728$</td>
<td>3.745</td>
<td>3.048</td>
<td>0.186</td>
<td>-0.232$^d$</td>
</tr>
<tr>
<td>1b</td>
<td>$J = 1$</td>
<td>$-70.54056 \pm 0.34737$</td>
<td>3.745</td>
<td>3.048</td>
<td>0.186</td>
<td>-0.232$^d$</td>
</tr>
<tr>
<td>2</td>
<td>$J = 0$</td>
<td>$-61.41945 \pm 0.31263$</td>
<td>3.983</td>
<td>2.743</td>
<td>0.044</td>
<td>-0.037$^c$</td>
</tr>
<tr>
<td>3</td>
<td>$J = 0$</td>
<td>$-56.05210 \pm 0.25881$</td>
<td>3.921</td>
<td>2.787</td>
<td>0.079</td>
<td>0.290</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>$-77.79686 \pm 0.35090$</td>
<td>3.717</td>
<td>3.092</td>
<td>0.174</td>
<td>-0.250</td>
</tr>
<tr>
<td>1a/1b</td>
<td>$J = 1$</td>
<td>$-76.60541 \pm 0.00409$</td>
<td>3.767</td>
<td>3.012</td>
<td>0.425</td>
<td>-0.009</td>
</tr>
<tr>
<td>2a/2b</td>
<td>$J = 1$</td>
<td>$-67.56110 \pm 0.00003$</td>
<td>3.739</td>
<td>3.060</td>
<td>0.048</td>
<td>-0.217</td>
</tr>
</tbody>
</table>

$^a$ Coriolis interactions included; the additional tunneling shift from eq 11 is given in parentheses. $^b$ Experiment: the value ($P_1(\cos \theta)) = 0.17 (\theta_1 = 80.2^\circ$) is obtained by correction of the experimental value of 0.191 for the induced dipole moment given by eq 17. $^c$ Experiment: the value ($P_2(\cos \theta)) = -0.069 (\theta_2 = 58.3^\circ$). $^d$ Experiment: the value ($P_2(\cos \theta)) = 0.069 (\theta_2 = 52.0^\circ$). $^e$ Experiment: the value ($P_2(\cos \theta)) = 0.069 (\theta_2 = 52.0^\circ$). $^f$ Experiment: the value ($P_2(\cos \theta)) = 0.069 (\theta_2 = 52.0^\circ$). $^g$ Experiment: the value ($P_2(\cos \theta)) = 0.069 (\theta_2 = 52.0^\circ$). $^h$ Experiment: the value ($P_2(\cos \theta)) = 0.069 (\theta_2 = 52.0^\circ$).

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Figure 3. Rotational branches of the lowest ($i = 0 \rightarrow 1$) van der Waals (internal rotor) $|0\rangle = 0 \rightarrow 1$ 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) $|0\rangle = 0 \rightarrow 1$ 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).

Figure 5. Rotational branches of the ($i = 1 \rightarrow 2$) van der Waals (internal rotor) $|1\rangle = 1 \rightarrow 1$ 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) (\times 10^6) m² s⁻¹ mol⁻¹</th>
<th>Q(2) (\times 10^6) m² s⁻¹ mol⁻¹</th>
<th>R(2) (\times 10^6) m² s⁻¹ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho (0 \rightarrow 1) ([\Omega] = 0 \rightarrow 1)</td>
<td>16.545 (16.415)⁴</td>
<td>77.59 (85.09)</td>
<td>412.33 (450.35)</td>
<td>359.54 (390.38)</td>
</tr>
<tr>
<td>ortho (0 \rightarrow 1) ([\Omega] = 0 \rightarrow 0)</td>
<td>26.533 (26.471)⁴</td>
<td>14.12 (12.82)</td>
<td>18.40 (16.30)</td>
<td>252.54 (211.78)</td>
</tr>
<tr>
<td>para (0 \rightarrow 1) ([\Omega] = 0 \rightarrow 1)</td>
<td>31.329 (34.318)⁴</td>
<td>186.09 (158.83)</td>
<td>18.40 (16.30)</td>
<td>252.54 (211.78)</td>
</tr>
<tr>
<td>para (0 \rightarrow 1) ([\Omega] = 0 \rightarrow 0)</td>
<td>1.346 (1.531)⁴</td>
<td>0.13 (0.13)</td>
<td>0.87 (0.93)</td>
<td>1.02 (1.16)</td>
</tr>
<tr>
<td>para (0 \rightarrow 1) ([\Omega] = 0 \rightarrow 1)</td>
<td>0.636 (0.737)⁴</td>
<td>0.01 (0.01)</td>
<td>0.19 (0.21)</td>
<td>0.42 (0.48)</td>
</tr>
<tr>
<td>para (0 \rightarrow 1) ([\Omega] = 0 \rightarrow 0)</td>
<td>10.383 (8.215)⁴</td>
<td>3.97 (4.30)</td>
<td>20.61 (22.32)</td>
<td>17.35 (18.80)</td>
</tr>
<tr>
<td>para (0 \rightarrow 1) ([\Omega] = 0 \rightarrow 0)</td>
<td>9.681 (7.434)⁴</td>
<td>3.01 (3.26)</td>
<td>15.67 (16.96)</td>
<td>13.27 (14.37)</td>
</tr>
<tr>
<td>para (0 \rightarrow 1) ([\Omega] = 1 \rightarrow 1)</td>
<td>9.045 (6.700)⁴</td>
<td>0.10 (0.10)</td>
<td>0.50 (0.54)</td>
<td>0.43 (0.46)</td>
</tr>
<tr>
<td>para (0 \rightarrow 1) ([\Omega] = 1 \rightarrow 0)</td>
<td>9.037 (6.683)⁴</td>
<td>0.09 (0.10)</td>
<td>0.49 (0.53)</td>
<td>0.42 (0.46)</td>
</tr>
</tbody>
</table>

*In parentheses: the intensity contribution from the permanent dipole. The Hönli-London factors for these transitions are P(2):Q(2):R(2) = 2:0:3 for \(\Omega = 0 \rightarrow 0\); 1:5:4 for \([\Omega] = 0 \rightarrow 1\); 9:5:16 for \([\Omega] = 1 \rightarrow 1\).° Experiment. ¹ Experiment. ² Experiment. ³ Experiment. ⁴ Experiment. ⁵ Experiment.

V that the absorption intensities are dominated by the permanent dipole on NH₃. The contributions from the dipole moments induced on Ar are only about ±10%. We do not show the figures with the spectra for the “bending” (\(i = 0 \rightarrow 2\)) and “stretch” (\(i = 0 \rightarrow 3\)) transitions in ortho NH₃-Ar since these spectra are very 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 flippness 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 (\([\Omega] = 0 \rightarrow 1\)) bands this intensity ratio is normal; it follows from the Hönli-London factors (see Table V). These factors arise directly from eq 21 if one keeps in mind that \(\Omega\) is a nearly good quantum number. For the \([\Omega] = 1 \rightarrow 1\) transitions in the para species the calculated P:Q:R intensity ratio does not correspond with the Hönli-London factors, however. It is closer to the ratio expected for \([\Omega] = 0 \rightarrow 0\) 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 \([\Omega] = 1 \rightarrow 1\) transitions to pick up intensity from the much stronger \([\Omega] = 0 \rightarrow 1\) 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 \(R_d\) 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 \(v_s\)

\[
D = 4B^3/v_s^2
\]

which has been derived for diatomics.²⁴,²⁷ 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 NH₃-Ar is strongly mixed with the stretch excitation. It seems from the expectation 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 NH₃-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.²⁷ It is found experimentally that the \([\Omega] = 0 \rightarrow 1\) transition from the ground state \((i = 0)\) to the 1a, 1b states in ortho dimers are about 30 times stronger than the \([\Omega] = 0 \rightarrow 1\) 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 observed²⁷ to be about 15 times stronger than the \([\Omega] = 1 \rightarrow 1\) 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 bands in Figure 3 and 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 \(\theta\). 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 \(\Omega = 0 \rightarrow 0\) and \([\Omega] = 1 \rightarrow 1\) bands and the perpendicular \([\Omega] =
Vibration–Rotation–Inversion Spectrum of Ar–NH$_3$

0–1 bands which follow from the calculations (cf. Figures 3–5), agree very well with the experimental data. Especially for the [0] = 1–1 band this is gratifying since the P:Q:R intensity ratio for this band deviates considerably from the kinematic Hönl–London factors, which implies that we describe the dynamics of this transition correctly.

Acknowledgment. We thank M. Bulski for providing Figure 1. We are grateful to W. L. Meerts, E. Zwart, R. J. Saykally, R. C. Cohen, and G. T. Fraser for making their results available before publication and to W. L. Meerts, W. Klemperer, and J. Reuss for stimulating discussions. Part of this work has been performed as an IBM/ACIS project.

Appendix

We shall consider in this Appendix how the different coordinates, introduced in the main text, transform under the molecular symmetry group $D_{3h}$. This group is generated by the permutations of the protons in NH$_3$ and the inversion $E^*$. The nuclei of the complex are at the points $H_1, H_2, H_3, N, C, and A$ (argon) in the Euclidean point space $E^3$. The center of mass of NH$_3$ is at C and that of the dimer at D.

Consider an arbitrary orthonormal right-handed space-fixed frame centered at $D$

$$\mathbf{e}_L = (e_L^x, e_L^y, e_L^z)$$
(A1)

With respect to this frame the point H$_1$ has the coordinate vector $H_1$ defined by $D(DH_1) = \mathbf{e}_L H_1$. Likewise we define the coordinate vectors $H_2, H_3, N, C, and A$ of $H_2, H_3, N, C,$ and $A$. Note that $CA$ is collinear with $DA$. Inversion $E^*$ of the total system with respect to the mass center $D$ maps a point $P$ with coordinate vector $P$ onto $P'$ with

$$E^* DP = DP' = \mathbf{e}_L (-P)$$
(A2)

Express $R$, the coordinate vector of $C_A$, in spherical polar coordinates

$$R = (R \sin \beta \cos \alpha, R \sin \beta \sin \alpha, R \cos \beta), \quad R = |CA|$$
(A3)

then from $E^* : R \rightarrow -R$ it follows that

$$E^* \alpha \rightarrow \alpha + \pi$$
$$E^* \beta \rightarrow \beta - \pi$$
(A4)

Using $\alpha$ and $\beta$, we define a right-handed dimer frame centered at $D$

$$\mathbf{e}_D = R(\alpha) R(\beta)$$
(A5)

where $R(\alpha)$ and $R(\beta)$ are the usual rotation matrices representing rotations around the $z$ and $y$ axis. In our convention, $R(\alpha) = -\sin \alpha$ and $R(\beta) = -\sin \beta$. The dimer frame transforms under $E^*$ as

$$E^* \mathbf{e}_D = R(\alpha + \pi) R(\beta)$$

Here we have used the relations

$$R(\alpha) R(\beta) = R(\beta) R(\alpha)$$
(A7)

$$R(\pi) R(\beta) = R(\beta) R(\pi)$$
(A8)

Obviously, the dimer frame is invariant under permutation of the protons.

Next we define a right-handed monomer frame at C

$$\mathbf{e}_C = (e_C^x, e_C^y, e_C^z)$$

and the inversion $E^*$ transforms the coordinate vector of the monomer at $C$ to $E^* R_C = \mathbf{e}_C R_C(\pi)$.

The vectors $(\mathbf{e}_C R_C)$ span the two-dimensional irrep $E$ of the permutation group $S_3 \subset PL(D_{3h})$ and $E^*$ spans the antisymmetric representation $A_2$ of this group. For the generators (123) and (23) we have therefore

$$(123) E^*_D = \mathbf{e}_D R_D(-2\pi/3)$$
(A10)

$$E^*_D = \mathbf{e}_D R_D(\pi)$$
(A11)

with $E^*_D = E^* e_D R_D$. In order to consider the effect of $E^*$ on $E^*_D$, we first observe that this frame is invariant under a change of origin, e.g.

$$E^*_C = \mathbf{e}_C R_C = \mathbf{e}_C R_C(\pi)$$
(A12)

The frame $E^*_C$ is not necessarily orthonormal. In the case of an ammonia molecule with $C_3v$ point group symmetry, which we obtain by imposing the constraints

$$\theta = \arccos \left(\frac{1}{2} \left(\frac{\rho_1 - \rho_2}{\rho_1 + \rho_2}\right)^2\right)$$

where $\rho_1$ and $\rho_2$ are the two basis vectors.

The frame $E^*_C$ is orthonormal, however, and the basis vectors can be normalized. The normalization factors of $f_2$ and $f_3$ 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., $f_2$ is the 3-fold axis, and that the frame $E^*_C$ is orthonormal.

We define the NH$_3$ inversion coordinate $\rho$ as the inner product of two collinear vectors

$$\rho = \langle C\bar{N}, f_2 \rangle$$
(A14)

Since $C\bar{N}$ is invariant under permutations of the protons, $\rho$ inherits its permutational properties from $f_2$, i.e., $\rho$ transforms as $A_2$ of $S_3$. In order to consider the effect of $E^*$, we evaluate the inner product of eq A14 in the space-fixed basis at $D$

$$\rho = \langle C\bar{N}, f_2 \rangle$$
(A15)

and, since $\rho$ is invariant under translation as well as under inversion (cf. eq A12), we find $E^* \rho = \rho$. The Euler angles of NH$_3$ with respect to the dimer frame are defined by the relation

$$\mathbf{e}_D = \mathbf{e}_C R_C(\gamma) R_C(\theta) R_C(\phi)$$
(A16)

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

$$\mathbf{e}^* D = \mathbf{e}^* C = \mathbf{e}_C R_C(\gamma) R_C(\theta) R_C(\phi)$$
(A17)

so that the Euler angles $\theta$ and $\gamma$ are the polar angles of the symmetry axis $f_2$ 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)

$$\mathbf{e}_D R_C(\pi) = \mathbf{e}_C^* D = \mathbf{e}_C R_C(\gamma') R_C(\theta') R_C(\phi')$$
(A18)

where $\gamma', \theta'$, and $\phi'$ are the transformed Euler angles. From eq
A18 and by the use of eqs A7 and A8 (and the corresponding equations with \( x, y, \) and \( z \) permuted), we find

\[
\mathbf{T}_0 = \mathbf{R}_{\gamma}(-\gamma) \mathbf{R}_{\pi}(-\phi) \mathbf{R}_{\phi}(\phi') \quad (A19) 
\]

Since Euler angles give a unique parametrization of an orthogonal matrix we may conclude that

\[
\mathbf{T}_0 = \begin{bmatrix}
\gamma & \gamma \\
\phi & \phi \\
\end{bmatrix} 
\]

(A20)

In the same manner by eq A11,

\[
\mathbf{T}_0 \mathbf{R}_s(\pi) = (23) \mathbf{T}_0 
\]

(A21)

whence

\[
\begin{align*}
\gamma &\rightarrow \gamma \\
\phi &\rightarrow \pi + \phi \\
\end{align*} \quad (23) \quad (A22) 
\]

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, \( \text{N}^\equiv\text{C}^\equiv\text{C}^\equiv\text{N} \)), both experimental4-6 and theoretical,7-9 have been made before. Based on partial photoionization cross section and photoelectron angular distribution parameter calculations.