Ab initio investigation of the bound rovibrational states in the electronic ground state of HeN$_2^+$

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The two-dimensional interaction potential of the N$_2^+$ ($X^2\Sigma_g^+$)–He (X $^1S$) system has been calculated using highly correlated ab initio MCSCF-CI wave functions for a fixed value of the N$_2^+$–He bond length (2.110 $a_0$). It is found to have a minimum about 140 cm$^{-1}$ below the N$_2^+$+He dissociation limit, significantly deeper than the minimum in the neutral system N$_2$–He. This well depth is enough to give rise to a cluster-like, bound structure with a considerable number of vibration–rotation levels in the electronic ground state. The well depth is almost independent of the N$_2$–He angle, which leads to large amplitude bending motions.

Rovibrational calculations have been performed on the surface for $J = 0, 1, 2$. Values for the rotational constant $B$, the fundamental stretching frequency $\nu_s$, and its first and second overtones, and the rotational constant $C_u$ in each $n\nu_s$ manifold, have been obtained from the energy levels computed. It is found that $B = 1.879$ cm$^{-1}$, $\nu_s = 55.231$ cm$^{-1}$, $2\nu_s = 83.404$ cm$^{-1}$, $3\nu_s = 92.491$ cm$^{-1}$, $C_0 = 0.477$ cm$^{-1}$, $C_1 = 0.370$ cm$^{-1}$, and $C_2 = 0.254$ cm$^{-1}$.

Estimates of the accuracy of these parameters are made.

I. INTRODUCTION

So far, comparatively little is known about the interaction potentials between molecular ions and atoms. It is expected that, in general, the attractive ion–induced dipole interaction leads to deeper potential minima than for the corresponding neutral systems, and that the increased well depth might give rise to large orbiting cross sections. It is thus possible that many stable clusters, with bound rovibrational states, could exist.

The ability of helium to form charged cluster compounds with several diatomic gases has been known for some time and recently the collision dynamics of the N$_2^+$–He system have been the subject of experimental studies. Katayama and co-workers$^2,3$ investigated the electronic energy transfer of excited N$_2^+$ ($A^2\Pi_u, v = 4$) into the rotational manifold of the $X^2\Sigma_g^+$ ($v = 8$) state in collision with helium. Dressler, Meyer, and Leone$^4$ have studied rotational alignment of N$_2^+$, in the electronic ground state, drifting in a helium buffer gas. Their work reported, for the first time, the detection of rotational alignment in charged species.

Most recently, Kriegel et al.$^5$ have measured the vibrational excitation of N$_2^+$ ions in collisions with He from the detected threshold to relative collisional energies of about 0.8 eV. The work of Kriegel et al. also suggests that the N$_2^+$–He cluster is bound. This would accord with recent ab initio studies of the H$_2^+$–He interaction$^6,7$, which have indicated a minimum in the potential energy surface, corresponding to the cluster HeH$_2^+$, 0.25 eV (2000 cm$^{-1}$) below the lowest dissociation limit, and for which bound rovibrational energy levels have been calculated.8

Encouraged by these results and the other dynamical studies, we have investigated the N$_2^+$ ($X^2\Sigma_g^+$)–He ($X^1S$) cluster theoretically. We have calculated the two-dimensional interaction potential using highly correlated ab initio multiconfiguration-reference configuration expansions (MCSCF-CI). The potential is found to have a minimum about 140 cm$^{-1}$ below dissociation. This is significantly deeper than the minima in the neutral system N$_2$–He$^9,10$ and in the isoelectronic CN–He$^{11}$ system. It is shown in the present paper that this well depth is enough to give rise to a cluster-like, bound structure with a considerable number of vibrational–rotational levels in the electronic ground state.

It is the purpose of the present work to introduce the ab initio interaction potential surface and to compute the vibrational–rotational bound states of HeN$_2^+$. Rotational alignment effects and collision induced electronic energy transfer between the $A^2\Pi_u$ and $X^2\Sigma_g^+$ states will be investigated in subsequent papers.12

II. N$_2^+$–He INTERACTION POTENTIAL

The potential energy function for N$_2^+$ ($X^2\Sigma_g^+$) + He ($X^1S$) was calculated using internally contracted ab initio MCSCF-CI$^{11}$–15 wave functions. The Gaussian basis set employed for the nitrogen atoms consisted of the Huzinaga$^{16,17}$ 11s, 7p basis set, augmented by three d and one f function for each atom with exponents 2.2, 0.66, 0.22, and 0.4, respectively. The 5s and 3p functions with the largest exponents were contracted. For helium we employed the Huzinaga$^{16,17}$ 7s basis (4s contracted), augmented by three p functions with exponents 1.2, 0.4, 0.13 and one d function with exponent 0.25. The basis set, set A, is given below Table II.

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Some test calculations for fixed values of \( R, r, \) and \( \theta \) were performed to study the effect of varying the size of the basis set. Here, \( R \) describes the distance from the atom to the center of mass of the diatomic, \( r \) is the bond length of the \( N_2^+ \) molecule, and \( \theta \) is the angle between \( R \) and \( r \). The molecular bond length was kept fixed at a value of \( r = 2.110 \ a_0 \) which is the mean distance in the vibrational ground state.

For \( R = 7.0 \ a_0, r = 2.110 \ a_0, \) and \( \theta = 0^\circ \) the interaction energy for \( N_2^+ + \) He is calculated with the above basis set to be \(-0.453 \ 08 \times 10^{-3} \ E_h \). Removing the \( f \) function on the N atoms and the \( d \) function on He (set B) yields a somewhat smaller attraction of \(-0.426 \ 43 \times 10^{-3} \ E_h \). This change value only slightly to \(-0.425 \ 70 \times 10^{-3} \ E_h \) if four \( d \) functions (exponents: \( 2.7, 0.9, 0.3, 0.1 \)) on N and four \( p \) functions (exponents: \( 1.8, 0.6, 0.2, 0.066 \)) on He were used. A more compact basis set containing only two \( d \) (exponents: \( 2.7 \)) and two \( p \)-polarization function (exponents: \( 0.85, 0.2 \)) results in an energy of \(-0.420 \ 01 \times 10^{-3} \ E_h \). The effect of adding more diffuse \( s \) and \( p \) functions on nitrogen or varying the exponents was found to be similarly small (1 to \( 3 \times 10^{-6} \ E_h \)).

The MCSCF-CI wave functions included all configurations which are singly or doubly excited relative to the MCSCF reference wave function. The reference configurations are listed in Table I. The orbitals were fully optimized in an MCSCF procedure.\(^{18-21} \) In order to reduce the basis superposition error the usual counterpoise correction\(^{22} \) was made. For this the energies of the subsystems \( N_2^+ \) and He have to be calculated at each geometry with the same basis set as that employed for the total system. The interaction energy is then obtained as \( \Delta E = E(N_2^+-\text{He}) - E(N_2^+) - E(\text{He}) \). The difference between the counterpoise corrected and uncorrected potentials is small, about \( 5\% \), in both the region of the minimum and in the repulsive part.

A further correction was, however, necessary. Due to the fact that the MCSCF-CI wave functions are not size consistent the interaction energy \( \Delta E \) does not vanish at large distances, i.e., at \( R = 100 \ a_0 \). Therefore, we subtracted \( \Delta E(R = 100) \) from \( \Delta E \) at all geometries, assuming that the size consistency error is constant as a function of the geometry. The calculated interaction energies are listed in Table II and plotted in Figs. 1 and 2.

The potential was fitted as described in Ref. 12. For the angular dependence we employed the usual Legendre polynomial expansion. To obtain the correct parameters for the Legendre expansion, the \( R \) dependence of the polynomial was represented by functions of the form

\[
B_\theta(R) = \exp(-a^\theta R) \left[ \sum_{i=0}^5 a^\theta_{i+2} R^i \right] - \tanh(R) \left[ \sum_{i=2}^4 C^\theta_i R^{-2i} \right]
\]

(1)

For \( \theta = 0^\circ, 45^\circ, \) and \( 90^\circ \). This was then expressed as a Legendre expansion with \( \lambda = 0, 2, \) and \( 4 \). Values of the \( a^\theta \) and \( C^\theta \) for set A are given in Table III.

From the analytic representation of the potential, the parameters \( e^\theta \) (well depth), \( R_e^\theta \) (position of \( e^\theta \)), and \( \sigma^\theta \) [value of \( R \) for which \( \nu(R,\theta) = 0 \)] were determined. These values are listed in Table IV. The well depth is about ten times deeper than in the neutral \( N_2 + \) He system,\(^9,10 \) and \( R_e \) and \( \sigma \) are 1.4 to 1.6 \( a_0 \) smaller. The anisotropy of both potentials is of similar magnitude.

### III. Calculation of Rovibrational Energy Levels

The coupled rotation–vibration energy levels for the \( \text{HeN}_2^+ \) cluster were calculated using the scattering coordinate approach and the programs TRIATOM and ROTLEV.

### Table II. Calculated interaction potential energy surface for the \( \text{HeN}_2^+ \) electronic ground state (in atomic units).

<table>
<thead>
<tr>
<th>( R )</th>
<th>( \nu(R,0^\circ) )</th>
<th>( \nu(R,45^\circ) )</th>
<th>( \nu(R,90^\circ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>7.3970( - 2)</td>
<td>3.5431( - 2)</td>
<td>2.0650( - 2)</td>
</tr>
<tr>
<td>4.0</td>
<td>2.8327( - 2)</td>
<td>1.3035( - 2)</td>
<td>5.9226( - 3)</td>
</tr>
<tr>
<td>4.5</td>
<td>9.5115( - 3)</td>
<td>3.5201( - 3)</td>
<td>1.0064( - 3)</td>
</tr>
<tr>
<td>5.0</td>
<td>2.2261( - 3)</td>
<td>2.9016( - 4)</td>
<td>3.7041( - 4)</td>
</tr>
<tr>
<td>5.5</td>
<td>6.4101( - 5)</td>
<td>5.7422( - 4)</td>
<td>6.1171( - 4)</td>
</tr>
<tr>
<td>6.0</td>
<td>5.8105( - 4)</td>
<td>6.2376( - 4)</td>
<td>5.4459( - 4)</td>
</tr>
<tr>
<td>6.5</td>
<td>5.7217( - 4)</td>
<td>5.1384( - 4)</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>4.5308( - 4)</td>
<td>3.8975( - 4)</td>
<td>3.2211( - 4)</td>
</tr>
<tr>
<td>8.0</td>
<td></td>
<td>2.1820( - 4)</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>1.4499( - 4)</td>
<td>1.2870( - 4)</td>
<td>1.1327( - 4)</td>
</tr>
<tr>
<td>12.0</td>
<td>3.9410( - 5)</td>
<td>3.6850( - 5)</td>
<td>3.4420( - 5)</td>
</tr>
<tr>
<td>15.0</td>
<td>1.5000( - 5)</td>
<td>1.4470( - 5)</td>
<td>1.3880( - 5)</td>
</tr>
<tr>
<td>20.0</td>
<td>4.5400( - 6)</td>
<td>4.4300( - 6)</td>
<td>4.3400( - 6)</td>
</tr>
<tr>
<td>25.0</td>
<td>1.8100( - 6)</td>
<td>1.7800( - 6)</td>
<td>1.7700( - 6)</td>
</tr>
</tbody>
</table>

*These energies have been corrected for basis superposition and size consistency errors. The GTO basis set, set A, comprised: N: \( s = 23 \ 274.857 \ 00(0.000 \ 215) \), \( 3468.183 \ 00(0.001 \ 692) \), \( 777.988 \ 43(0.008 \ 994) \), 215.719 76(0.037 730), 68.079 08(0.126 717), 23.424 40.8.669 38, 3.421 75.0.931 26, 0.346 57.0.133 12; \( p: 60.317 \ 24(0.003 \ 977) \), 14.100 81(0.027 642), 4.387 72(0.108 102), 1.608 27.0.638 85.0.260 36.0.103 97; \( d: 2.2000 \ 0.6600 \ 0.2200; f: 0.4000 \); He: \( s = 4.416 \ 464.50(0.001 \ 270), 6.242 \ 15 \ 0.009 \ 710), 14.221 \ 23(0.047 \ 270), 4.038 \ 78(0.158 \ 150), 1.297 18.0.447 53, 0.160 27; p: 1.2000 \ 0.4000 \ 0.1300; d:0.2500 \) (contraction coefficients given in parentheses).

*Values in parentheses are powers of 10.
which have been documented elsewhere.\textsuperscript{23–25} For the counterpoise and size consistency corrected potential calculated with the full basis set, set A (which we shall refer to as Pot. I), energy levels were calculated for values of the total angular momentum of the system \( J \) equal to 0, 1, and 2. We have not calculated fine interactions.

In order to get an indication of the accuracy of our calculations energy levels have also been computed using two further surfaces—the uncorrected potential calculated from basis set A (Pot. II) and the potential calculated from the more compact basis set, set B, corrected for size consistency and superposition effects (Pot. III).\textsuperscript{26} For these potentials calculations were performed only for \( J = 0 \) and 1.

Since the minimum in the potential with respect to dissociation of the cluster is an order of magnitude less than the energy required to excite the fundamental vibration of \( \text{N}_2^+ \), computations for these three potentials were carried out with the diatomic bond length \( r \) fixed at its equilibrium value of 2.11\( \text{a}_0 \). The molecular \( z \) axis was fixed along the scattering coordinate \( R \) joining the center of the \( \text{N}_2 \) bond to the He atom. We also tested the effect of varying the diatomic bond length, computing energy levels for \( r \) reduced by 10\%, for the full potential Pot. I.

A basis set consisting of 35 Morse oscillator-like functions in \( R \) was used to represent the stretching vibrations of the cluster. The bending modes were represented by five Legendre polynomials—free rotor functions—to a maximum order of \( j = 8 \) or 9.

\begin{table}[ht]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & \( \theta = 0^\circ \) & \( \theta = 45^\circ \) & \( \theta = 90^\circ \) \\
\hline
\( a_1 \) & 0.315 948 323 7( +1) & 0.192 514 029 9( +1) & 0.176 120 755 0( +1) \\
\hline
\( a_2 \) & 0.670 786 823 7( +6) & 0.342 919 785 1( +3) & 0.481 010 068 4( +2) \\
\hline
\( a_3 \) & - 0.719 384 208 3( +6) & 0.274 920 194 4( +3) & 0.604 840 359 5( +2) \\
\hline
\( a_4 \) & 0.308 728 247 7( +6) & - 0.695 997 271 7( +2) & - 0.213 354 405 3( +2) \\
\hline
\( a_5 \) & - 0.665 728 303 7( +5) & 0.741 100 257 4( +1) & 0.335 060 489 8( +1) \\
\hline
\( a_6 \) & 0.722 702 903 2( +4) & - 0.290 179 574 3( +0) & - 0.248 597 299 5( +0) \\
\hline
\( a_7 \) & - 0.305 305 531 4( +3) & - 0.938 237 156 3( -3) & 0.692 506 106 4( -2) \\
\hline
\( C_1 \) & 0.676 890 163 8( +0) & 0.677 686 982 0( +0) & 0.683 304 020 1( +0) \\
\hline
\( C_2 \) & 0.180 428 107 3( +2) & 0.121 194 468 7( +2) & 0.460 840 346 6( +1) \\
\hline
\( C_3 \) & 0.337 273 280 0( +3) & 0.309 276 412 6( +2) & - 0.448 474 001 3( +2) \\
\hline
\end{tabular}
\caption{Potential coefficients for \( \text{N}_2^+ \)--\text{He} in atomic units, see Eq. 1. (Powers of 10 in parentheses.)}
\end{table}
TABLE IV. Potential parameters for $N_2^+$–He.

<table>
<thead>
<tr>
<th>$\theta$ (deg)</th>
<th>$\epsilon^a$ (cm$^{-1}$)</th>
<th>$R_{\min}^b$ (a$_0$)</th>
<th>$\sigma^c$ (a$_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>133.12</td>
<td>6.199</td>
<td>5.471</td>
</tr>
<tr>
<td>45</td>
<td>139.36</td>
<td>5.840</td>
<td>5.103</td>
</tr>
<tr>
<td>90</td>
<td>134.36</td>
<td>5.529</td>
<td>4.783</td>
</tr>
</tbody>
</table>

*e$: well depth; $R_{\min}$: position of minimum of the well; $\sigma$: the value of $R$ at which $V(R, \theta) = 0$.

The vibrational levels closest to dissociation are very diffuse and to converge the energies computed for these states it was necessary to integrate over the potential out to $14$ a$_0$. This was found sufficient to converge these levels to within $0.5$ cm$^{-1}$. For more strongly bound levels, the convergence improved with decreasing energy from $0.1$ cm$^{-1}$ at $8$ cm$^{-1}$ below dissociation to better than $0.001$ cm$^{-1}$ for the ground state.

In the present method, calculations using basis sets which have even values of $j$ assigned to the associated Legendre functions $\Theta_{j\lambda}$ are performed separately from those using $j$ odd basis functions. The resulting states are labeled $e$ and $o$, respectively. For $J > 0$, the rovibrational states are also labeled $e(p = 0)$ or $f(p = 1)$, giving the total parity of the wave function of $(-1)^{j+e}$. The $J > 0$ problem thus divides into four blocks which we label $ee$, $ef$, $oe$, and $of$.

IV. RESULTS

Energy levels for the vibrational band origins ($J = 0$) for the three potentials are presented in Table V. In each case the ground state energy is given relative to dissociation of the cluster, and the vibrational energy levels are given with respect to the ground state. It is possible to assign the computed rovibrational energy levels to two idealized models—either to the harmonic oscillator-rigid rotor or to the free rotor description.

In the harmonic oscillator model, band origins ($J = 0$ states) are assigned to quanta of the stretching and bending vibrations $\nu_s$ and $\nu_b$. In the absence of Coriolis coupling $k$, the projection of the total angular momentum $J$ on the molecule-fixed $z$ axis would also be a good quantum number.

In the free internal rotor model, $\nu_s$ is still the correct stretching quantum number, but $\nu_b$ and $k$ are inappropriate. Instead we use $j$ and $l$, where $l$ represents the orbital angular momentum of the cluster and $j$ the rotation of the diatomic.

The vector relation $J = j + l$ constrains the possible values of $l$ within a $v_s, j$ manifold. If the $HeN_2^+$ cluster behaved exactly as a free internal rotor, $J = 0$ states labeled $j$ would be composed solely of basis functions comprising $\Theta_{j0}(\cos \theta)$.

Since the well depth is almost independent of the $N_2$–He...
angle (Figs. 1 and 2), leading to large amplitude bending motions, the internal rotor description might be expected to give a good interpretation of the computed energy levels.

For the full basis set, corrected potential, Pot. I, our results give 15 states whose energy is below that of the dissociation point of the electronic potential, the highest being less than 0.1 cm$^{-1}$ below dissociation. There is a further state which comes from the $j$ odd levels, whose energy lies below that required to dissociate into He plus N$_2^+$ ($j = 1$) molecule.

Contour plots of some of the wave functions of these states are given in Figs. 3 and 4. Nodes in the $R$ coordinate give number of stretching quanta associated with the state, while nodes in the $\theta$ axis indicate the $j$ character derived from the basis functions.

The contour plots of most of the functions enable unambiguous assignments to $(\nu_3, j)$ states to be made, and these are also given in Table V. For the three highest levels with $j$ even, however, there is considerable state mixing and the assignments are ambiguous (Fig. 4). For example, analysis of the contributions from the $j$ subsets of the basis functions to the total wave function of the state labeled (3,0) shows that it is made up 40% of $j = 4$ basis functions, and it includes 33% from the $j = 2$ functions.

It is possible to envisage cuts taken in the respective contour plots parallel to the $\theta$ axis at various values of $R$. For the wave functions of all three highest $j$ states the nodal structure in $\theta$ thus produced is characteristic of higher $j$ modes for smaller values of $R$ (< 7 $a_0$) declining to almost no structure at all for values of $R$ > 12 $a_0$.

The uncorrected potential shows a deeper minimum, which results in the ground state being some 17 cm$^{-1}$ more bound than the fully corrected potential. This means that the (2,3) level now lies below the dissociation point of the electronic potential. A further difference between the two potentials is that the $R$ stretching vibrations are all higher in frequency than the corresponding levels in the full potential. This causes (2,0) to lie above (1,3) and (3,0) above (2,2).

For the small-basis potential, the ground state is only 85.8 cm$^{-1}$ below dissociation, giving just 13 bound states. Levels (2,2) and (0,6) are the absentees. In this potential the $R$ stretching modes occur at considerably lower frequencies than for the full potential.

Shortening $r$ by 10% also reduces the number of bound states to 13, (2,2) and (0,6) again being absent. In this case, however, this is not due to the ground state being significantly closer to dissociation—the difference in this level due to changing the value of $r$ is less than 0.1 cm$^{-1}$—but because the shorter N$_2^+$ bond length leads to a significant increase in the value of the rotational constant. This also causes an accidental resonance between (0,4), frequency 54.941 cm$^{-1}$, and (1,0) frequency 55.433 cm$^{-1}$. Similar dependence on the diatomic rotational constant leading to a very irregular structure of the higher vibrational levels has been noted in the ArHCl van der Waals complex.  

In all four cases studied, the large anharmonicity of the $R$-stretching vibration is apparent—the frequency of the $2\nu_3$ mode being considerably less than twice that of the stretching fundamental. For the full potential, $\nu_3$ is only 11.3 cm$^{-1}$ above $2\nu_3$, compared to a fundamental $\nu_3$ of 55.2 cm$^{-1}$.

In the absence of sufficient data to carry out a full fit to obtain the various rovibrational parameters, we have calculated the “theoretical” free rotor energies of the levels according to the formula:

$$\omega = n\nu_3 + 2B(j + 1) + 2C_n(l + 1),$$

where the value of $B$ is simply taken from the $n = 0, j = 1$, $l = 0$ level in the $J = 1$ manifold (Table VI); $n\nu_3$ is given by the appropriate band origin; and $C_n$ in each $n\nu_3$ manifold is obtained from the $n\nu_3, J = 0, l = 1$ level in the $J = 1$ manifold.

Thus we have $B = 1.879$ cm$^{-1}$, $1\nu_3 = 55.231$ cm$^{-1}$, $2\nu_3 = 83.404$ cm$^{-1}$, $3\nu_3 = 92.491$ cm$^{-1}$, $C_0 = 0.477$ cm$^{-1}$, $C_1 = 0.370$ cm$^{-1}$, and $C_2 = 0.254$ cm$^{-1}$. Similarly, we have used the computed lowest $\nu_3$ state to calculate higher levels for the harmonic oscillator model—the $n\nu_3$ energy again being taken to be as computed. This gives us a value of $\nu_3 = 5.645$ cm$^{-1}$.

Comparison of the free rotor and harmonic oscillator models for the $J = 0$ levels is shown in Fig. 5, where predict-
TABLE VI. Free rotor assignments for the computed rovibrational levels. All frequencies are given in cm\(^{-1}\) relative to the \(J = 0\) ground state at \(-97.817\) cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Assignment</th>
<th>(J = 0)</th>
<th>(J = 1)</th>
<th>(J = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu, j)</td>
<td>(\omega_{\text{calc}})</td>
<td>(\omega_{\text{PR}})</td>
<td>(\omega_{\text{calc}})</td>
</tr>
<tr>
<td>0 0</td>
<td>0.0 0.0 0.0</td>
<td>1 0.954 0.954</td>
<td>2 2.861 2.861</td>
</tr>
</tbody>
</table>

*Unbound states.

terms of the free rotor assignments for \(J > 0\).

The computed energy levels for \(J = 0, 1,\) and 2 for the full potential are compared with those predicted by Eq. (2) in Table VI. We have also calculated the value of \(\gamma\), the Yamada–Winnewisser parameter,\(^{28,29}\) which gives a measure of the extent to which a free rotor description is appropriate. For an ideal free internal rotor \(\gamma\) should have the value of \(-3\).

Given the simplicity of the model used to calculate the theoretical free rotor energy levels, e.g., we have made no allowance for centrifugal distortion, it fits the calculated energies remarkably well. For those levels for which we have sufficient data to compute it, \(\gamma\) approaches \(-3\), varying between \(-2.3\) and \(-2.8\).

In previous studies of van der Waals clusters, there has been an assumption that Coriolis coupling, mixing basis functions from \(k\) subsets to \(k+1\) functions, is unimportant.\(^{30,31}\) Our results for this particular system indicates that this is not a good approximation. For example, the second level in the \(J = 2ee\) block (computed energy 11.458 cm\(^{-1}\)) is expected in the no Coriolis assumption to have a value of \(k = 2\). But \(k = 2\) basis functions contribute only 52% to this state. Moreover—with the exception of states assigned to the \(\nu_1\) manifold—Coriolis coupling becomes generally more significant with increasing energy. As a result \(k > 1\) \(e\) and \(f\) levels
which should be degenerate are considerably split.

The ground state vibrational energies listed in Table V indicate that the full, corrected potential, \( \text{Pot. I} \), could underestimate the dissociation energy by 10%. This would have the effect of altering the shape of the potential well, lowering the value of the second derivative with respect to \( R \). As a result, we estimate that the stretching frequency \( \nu_s \) could be about 10% too low.

The value of \( C_0 \) obtained for Pot. II from the \( J = 1, j = 0, l = 1 \) level is 0.49 cm\(^{-1}\), however, just 4% greater than that for Pot. I, while for Pot. III \( C_0 \) is 0.460 cm\(^{-1}\), 4% lower. The corresponding values of \( B \) are, respectively, 0.5% and just under 2% higher. It can be expected, therefore, that the relative energy differences of rotational states within a given vibrational band can be accurate to within about 5%. At the same time, accidental degeneracies which could seriously perturb the characteristics of the rovibrational modes cannot be ruled out.

We have also calculated the dipole moment of the \( \text{HeN}_2^+ \) cluster relative to the center of mass. For \( R = 5.5 a_0 \) and \( \theta = 0^\circ \), for instance, the dipole moment is 1.51 D. This is a fairly large value, and may lead to rovibrational transitions within the electronic ground state being spectroscopically observable. However, the ground state rotation–vibration energy levels might be better monitored by the detection of shifts in the \( B-X \) electronic transition of \( \text{N}_2^+ \). The potential energy function for the corresponding cluster is currently being computed.

V. CONCLUSIONS

Bound rotation–vibration levels of the \( \text{HeN}_2^+ \) cluster have been predicted from a two-dimensional \textit{ab initio} MCSCF-CI potential energy function. The large amplitude quantised bending modes are well described in terms of the free internal rotor model. This is in marked contrast with the more tightly bound \( \text{HeH}_2^+ \) cluster for which a linear geometry was found with a large barrier to internal rotation.\(^8\)

For the best basis set used for \( \text{HeN}_2^+ \) we find at least 15 vibrational band origins lie below the dissociation limit (97.8 cm\(^{-1}\)). The stretching vibrational frequencies have been calculated with an expected accuracy of about 10%. Within each \( \nu_s \) manifold, however, the rotational term values are expected to have an accuracy of about 5%.

It is hoped that the results will assist spectroscopic investigations of this species, either in its electronic ground state or via perturbed \( X-B \) transitions of \( \text{N}_2^+ \).

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