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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^+ 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, and 2. Values for the rotational constant B, the fundamental stretching frequency ν_s, and its first and second overtones, and the rotational constant C_n in each $n\nu_s$ manifold, have been obtained from the energy levels computed. It is found that $B = 1.879$ cm^{-1}, $1\nu_s = 55.231$ 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[1] 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 exctitation of N_2^+ ions in collisions with He from the detected threshold to relative collisional energies of about 0.8 eV. The work of Kreigel *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[13–15] wave functions. The Gaussian basis set employed for the nitrogen atoms consisted of the Huzinaga[16,17] 11*s*, 7*p* 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 5*s* and 3*p* functions with the largest exponents were contracted. For helium we employed the Huzinaga[16,17] 7*s* basis (4*s* 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 θ 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 θ is the angle between $\mathbf{R}$ and $\mathbf{r}$. 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 $\theta = 0°$ 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 value changed 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: 0.2) 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 3×10^{-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 $\Delta E = E(N_2^+\text{–}He) - E(N_2^+) - E(He)$. 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 ΔE does not vanish at large distances, i.e., at $R = 100\ a_0$. Therefore, we subtracted $\Delta E(R = 100)$ from ΔE 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

$$B_\theta(R) = \exp(-a_1^\theta R)\left[\sum_{i=0}^{5} a_{i+2}^\theta R^{i}\right] - \tanh(R)\left[\sum_{i=2}^{4} C_{2i}^\theta R^{-2i}\right] \tag{1}$$

for $\theta = 0°$, 45°, and 90°. This was then expressed as a Legendre expansion with $\lambda = 0$, 2, and 4. Values of the a_i^θ and C_i^θ for set A are given in Table III.

From the analytic representation of the potential, the parameters ϵ^θ (well depth), R_m^θ (position of ϵ^θ), and σ^θ [value of R for which $V(R,\theta) = 0$] 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_m and σ 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 HeN_2^+ cluster were calculated using the scattering coordinate approach and the programs TRIATOM and ROTLEV,

TABLE I. MCSCF reference configurations used in the MCSCF-CI calculations for $N_2^+ + He$. The configurations are given for collinear geometries.[a]

No.	$^2\Sigma^+$
1	$5\sigma^2 6\sigma 1\pi_x^2 1\pi_y^2$
2	$5\sigma^2 6\sigma 1\pi_x^2 2\pi_y^2$
3	$5\sigma^2 6\sigma\, 2\pi_x^2 1\pi_y^2$
4[b]	$5\sigma^2 6\sigma S(1\pi_x,2\pi_x) S(1\pi_y,2\pi_y)$
5	$6\sigma^2 5\sigma S(1\pi_x,2\pi_x) 1\pi_y^2$
6	$6\sigma^2 5\sigma T(1\pi_x,2\pi_x) 1\pi_y^2$
7	$6\sigma^2 5\sigma S(1\pi_y,2\pi_y) 1\pi_x^2$
8	$6\sigma^2 5\sigma T(1\pi_y,2\pi_y) 1\pi_x^2$

[a] In C_s symmetry, σ and π_x orbitals become a', and the π_y orbitals, a''. The orbitals 1σ–4σ are doubly occupied in all configurations. The He 1s orbital is 4σ.

[b] $S(a,b)$,$T(a,b)$ indicate, respectively, singlet and triplet coupling of the two electrons in parentheses.

TABLE II. Calculated interaction potential energy surface for the HeN_2^+ electronic ground state (in atomic units).[a]

R	$V(R,0°)$	$V(R,45°)$	$V(R,90°)$
3.5	7.3970(− 2)[b]	3.5431(− 2)	2.0650(− 2)
4.0	2.8327(− 2)	1.3035(− 2)	5.9226(− 3)
4.5	9.5115(− 3)	3.5201(− 3)	1.0084(− 3)
5.0	2.2261(− 3)	2.9016(− 4)	− 3.7041(− 4)
5.5	− 6.4310(− 5)	− 5.4722(− 4)	− 6.1171(− 4)
6.0	− 5.8105(− 4)	− 6.2376(− 4)	− 5.4459(− 4)
6.5	− 5.7217(− 4)	− 5.1384(− 4)	
7.0	− 4.5308(− 4)	− 3.8975(− 4)	− 3.2211(− 4)
8.0		− 2.1820(− 4)	
9.0	− 1.4499(− 4)	− 1.2870(− 4)	− 1.1327(− 4)
12.0	− 3.9410(− 5)	− 3.6850(− 5)	− 3.4420(− 5)
15.0	− 1.5090(− 5)	− 1.4470(− 5)	− 1.3880(− 5)
20.0	− 4.5400(− 6)	− 4.4300(− 6)	− 4.3400(− 6)
25.0	− 1.8100(− 6)	− 1.7800(− 6)	− 1.7700(− 6)

[a] These energies have been corrected for basis superpositon 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), 68.078 03(0.126 671), 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: 414.466 50(0.001 270), 62.249 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: 1.2000,0.4000,0.13000; d:0.2500 (contraction coefficients given in parentheses).

[b] Values in parentheses are powers of 10.

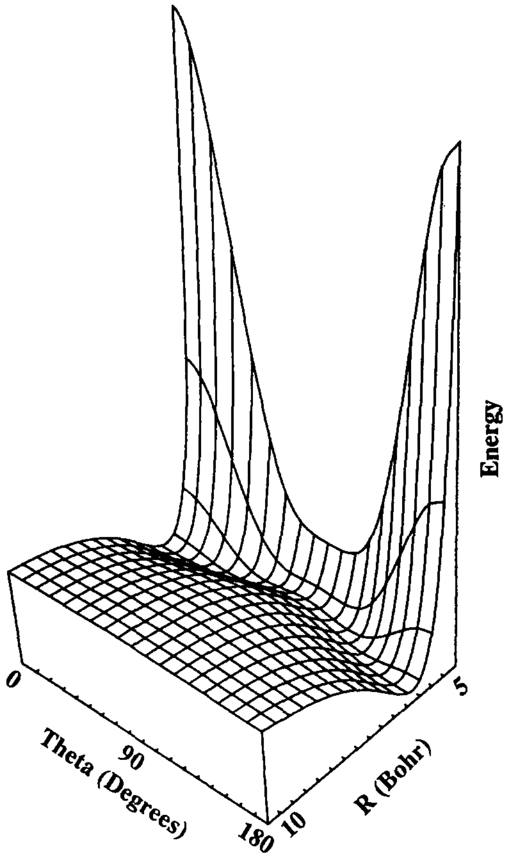

FIG. 1. Interaction potential energy surface (Pot. I) for N_2^+–He as a function of distance R between the N_2^+ bond center and He, and the angle θ between R and the N_2^+ bond. (Energy in arbitrary units.)

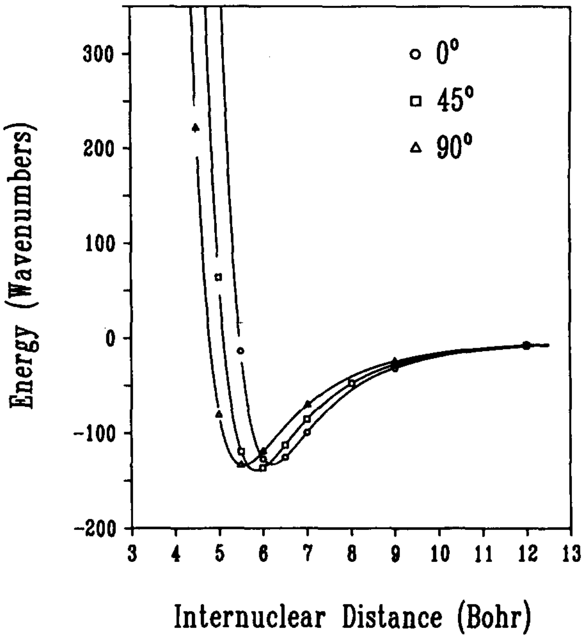

FIG. 2. Interaction potential energy surface (Pot. I) for N_2^+–He as a function of R for fixed values of $\theta = 0°$, 45°, and 90°.

which have been documented elsewhere.[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).[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 N_2^+, computations for these three potentials were carried out with the diatomic bond length r fixed at its equilibrium value of 2.110 a_0. The molecular z axis was fixed along the scattering coordinate R joining the center of the 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.

TABLE III. Potential coefficeints for N_2^+–He in atomic units, see Eq. (1). (Powers of 10 in parentheses.)

	$\theta = 0°$	$\theta = 45°$	$\theta = 90°$
a_1^θ	0.315 948 323 7(+ 1)	0.192 514 029 9(+ 1)	0.176 120 755 0(+ 1)
a_2^θ	0.670 786 823 7(+ 6)	− 0.342 919 785 1(+ 3)	− 0.481 010 068 4(+ 2)
a_3^θ	− 0.719 384 208 3(+ 6)	0.274 920 194 4(+ 3)	0.604 840 359 5(+ 2)
a_4^θ	0.308 728 247 7(+ 6)	− 0.695 997 271 7(+ 2)	− 0.213 354 405 3(+ 2)
a_5^θ	− 0.665 298 303 7(+ 5)	0.741 100 257 4(+ 1)	0.335 060 489 8(+ 1)
a_6^θ	0.722 702 903 2(+ 4)	− 0.290 179 574 3(+ 0)	− 0.248 597 299 5(+ 0)
a_7^θ	− 0.305 305 531 4(+ 3)	− 0.938 237 156 3(− 3)	0.692 506 106 4(− 2)
C_4^θ	0.676 890 163 8(+ 0)	0.677 686 982 0(+ 0)	0.683 304 020 1(+ 0)
C_6^θ	0.180 428 107 3(+ 2)	0.121 194 468 7(+ 2)	0.460 840 346 6(+ 1)
C_8^θ	0.337 273 280 0(+ 3)	0.309 276 412 6(+ 2)	− 0.448 474 001 3(+ 2)

TABLE IV. Potential parameters[a] for N_2^+-He.

θ(deg)	$\epsilon^\theta(\mathrm{cm}^{-1})$	$R_m^\theta(a_0)$	$\sigma^\theta(a_0)$
0	− 133.12	6.199	5.471
45	− 139.36	5.840	5.103
90	− 134.36	5.529	4.783

[a] ϵ^θ: well depth; R_m^θ: position of minimum of the well; σ^θ: 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 $\Theta_{j,k}$ 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 $(-1)^{J+p}$. 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.

TABLE V. Band origins ($J = 0$) for HeN_2^+ calculated with different potential energy surfaces.

Assignment $v_s j$	Computed frequencies[a] (cm^{-1}) Pot I	Pot II	Pot III[b]
0 0	− 97.817	− 114.536	− 85.782
0 1	5.645	5.197	4.564
0 2	16.000	17.636	14.283
0 3	28.624	29.542	27.559
0 4	47.459	48.639	46.359
1 0	55.231	62.581	49.741
1 1	61.276	68.636	55.036
0 5	69.155	70.724	67.615[c]
1 2	70.278	78.517	64.007
2 0	83.404	95.694	74.124
1 3	83.418	91.101	80.728[c]
2 1	89.636	102.202	76.900
3 0	92.491[c]	110.553	84.283
2 2	94.703[c]	106.926	
0 6	97.719[c]	97.067	
2 3	100.148	108.606	

[a] Ground state energy given relative to dissociation. Band origins given relative to ground state.

[b] For details of potentials, see the text.

[c] These states are considerably mixed.

In the harmonic oscillator model, band origins ($J = 0$ states) are assigned to quanta of the stretching and bending vibrations ν_s and ν_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, ν_s is still the correct stretching quantum number, but ν_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 $\mathbf{J} = \mathbf{j} + \mathbf{l}$ constrains the possible values of l within a ν_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 $\Theta_{j,0}(\cos\theta)$.

Since the well depth is almost independent of the N_2–He

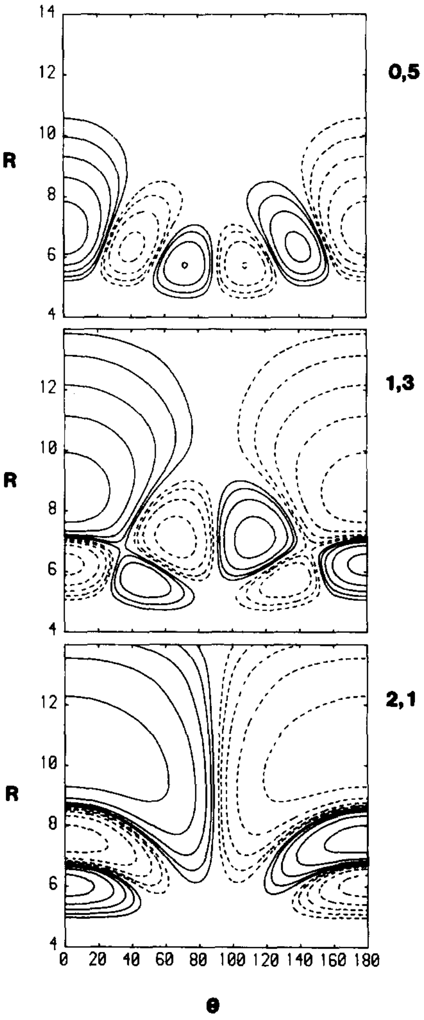

FIG. 3. Wave functions for the three highest bound states of HeN_2^+ with j odd as a function of R and θ. Top $v_s = 0, j = 5$, (0,5); middle (1,3); bottom (2,1). (2,1) is the last truly bound state for j odd. Contours link points 64%, 32%, 16%, 8%, and 4% of the maximum amplitude of the wave function. Solid (broken) curves enclose areas of positive (negative) amplitude. (R in bohr, θ in degrees.)

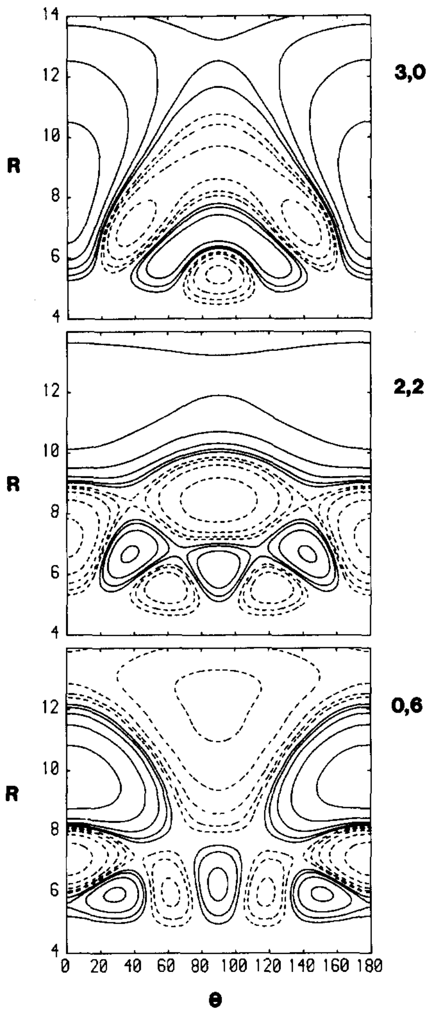

FIG. 4. Wave functions for the three highest bound states of HeN_2^+ with j even. Top (3,0); middle (2,2); bottom (0,6). (0,6) is the last truly bound state for j even. Contours as for Fig. 3.

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 θ axis indicate the j character derived from the basis functions.

The contour plots of most of the functions enable unambiguous assignments to (v_s, 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 θ axis at various values of R. For the wave functions of all three highest j even states the nodal structure in θ 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.[27]

In all four cases studied, the large anharmonicity of the R-stretching vibration is apparent—the frequency of the $2v_s$ mode being considerably less than twice that of the stretching fundamental. For the full potential, $3v_s$ is only 11.3 cm^{-1} above $2v_s$, compared to a fundamental v_s 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:

$$\omega = n v_s + 2Bj(j+1) + 2C_n l(l+1), \qquad (2)$$

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

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

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 $-97.817\ cm^{-1}$.

Assignment	$J = 0$			$J = 1$			$J = 2$			
$\nu_s\ j$ γ	l	ω_{calc}	ω_{FR}	l	ω_{calc}	ω_{FR}	l	ω_{calc}	ω_{FR}	γ
0 0	0	0.0	0.0	1	0.954	0.954	2	2.861	2.861	− 2.41
0 1	1	5.645	4.712	0	3.758	3.758	1	4.855	4.712	− 2.38
				1	4.375	4.712	2	6.332	6.620	
				2	7.153	6.620	3	9.792	9.482	
0 2	2	16.000	14.136	1	12.687	12.228	0	11.458	11.274	− 2.79
				2	13.836	14.136	1	12.078	12.228	
				3	18.040	16.998	2	14.579	14.136	
							3	16.692	16.998	
							4	21.405	20.814	
0 3	3	28.624	28.272	2	26.437	25.410	1	24.121	23.502	− 2.77
				3	29.455	28.272	2	25.282	25.410	
				4	32.532	32.088	3	28.153	28.272	
							4	32.667	32.088	
							5	36.965	36.858	
0 4	4	47.459	47.120	3	43.806	43.304	2	41.291	40.442	− 2.64
				4	47.099	47.120	3	44.014	43.304	
				5	51.612	51.890	4	47.697	47.120	
							5	51.732	51.890	
							6	57.488	57.614	
0 5	5	69.155	70.680	4	65.404	65.910	3	62.153	62.094	
				5	69.689	70.680	4	65.615	65.910	
				6	74.187	76.404	5	69.543	70.680	
							6	74.624	76.404	
							7	83.754	83.082	
0 6	6	97.719	98.952[a]	5	94.279	93.228	4	86.051	88.458	
							5	94.374	93.228	
							6	96.644	98.952[a]	
1 0	0	55.231	55.231	1	55.971	55.971	2	56.751	56.451	− 2.74
1 1	1	61.276	59.729	0	58.927	58.989	1	59.831	59.729	− 2.31
				1	59.292	59.729	2	60.790	61.209	
				2	62.314	61.209	3	64.337	63.429	
1 2	2	70.278	68.725	1	68.570	67.245	0	66.832	66.505	
				2	69.864	68.725	1	67.112	67.245	
				3	72.305	70.945	2	69.454	68.725	
							3	71.877	70.945	
							4	75.061	73.905	
1 3	3	83.418	82.219	2	81.571	79.999	1	79.608	78.519	
				3	83.608	82.219	2	81.641	79.999	
				4	85.863	85.179	3	80.288	82.219	
							4	86.118	85.179	
							5	89.217	88.879	
1 4				3	96.774	97.251	2	93.615	95.031	
2 0	0	83.404	83.404	1	83.912	83.912	2	84.917	84.928	− 2.43
2 1	1	89.636	87.670	0	88.004	87.162	1	87.884	87.670	
				1	88.458	87.670	2	89.993	88.686	
				2	90.951	88.686	3	89.217	90.210	
2 2	2	94.703	96.202	1	95.167	95.186	0	93.496	94.678	
				2	96.985	96.202	1	95.879	95.186	
							2	95.702	96.202	
3 0	0	92.491	92.491							

[a] Unbound states.

ed energy levels are correlated to those computed. It is clear that while the free rotor model used accounts fairly satisfactorily for the computed levels, the harmonic oscillator fails completely to give an accurate representation of our results. For this reason the computed levels are presented only in terms of the free rotor assignments for $J > 0$.

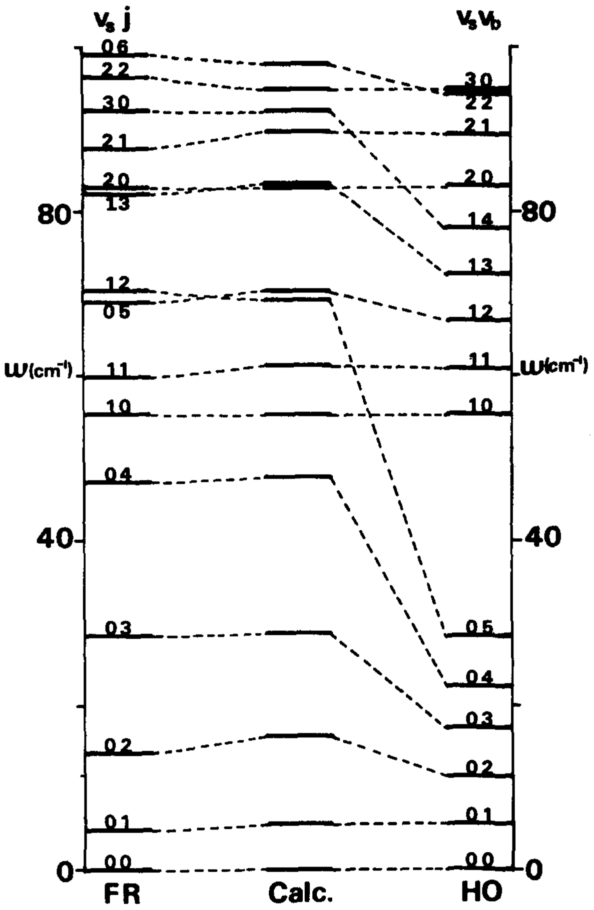

FIG. 5. Correlation of free rotor (FR) and harmonic oscillator (HO) energy levels with calculated energies for $J = 0$. [See Eq. (2) and the text for explanation of FR and HO parameters used.]

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 γ, 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 γ 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, γ 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 $k \pm 1$ 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 ν_s manifold—Coriolis coupling becomes generally more significant with increasing energy. As a result $k \geqslant 1$ 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, 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 derivitive with respect to R. As a result, we estimate that the stretching frequency ν_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 are 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 HeN_2^+ cluster relative to the center of mass. For $R = 5.5\ a_0$ and $\theta = 0°$, 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 N_2^+. The potential energy function for the corresponding cluster is currently being computed.

V. CONCLUSIONS

Bound rotation–vibration levels of the HeN_2^+ cluster have been predicted from a two-dimensional *ab initio* MCSCF-CI potential energy function. The large amplitude quantised bending modes are well described in terms of ta free internal rotor model. This is in marked contrast with the more tightly bound HeH_2^+ cluster for a which a linear geometry was found with a large barrier to internal rotation.[8]

For the best basis set used for 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 ν_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 N_2^+.

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