Theoretical Support for the Identification of the Microwave Line at 93·174 GHz as being due to the Molecular Ion N_2H^+

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Summary *Ab initio* calculations, including correlation effects, of the geometry of N_2H^+, provide very strong support for the identification of the microwave line at 93·174 GHz as being due this molecular ion.

INCREASING use is now being made of the results of *ab initio* molecular orbital calculations to identify interstellar molecules which have not been observed in the laboratory.[1,2] The interpretation of the microwave lines of such species requires calculations of molecular geometry of greater accuracy than is obtained at the Hartree–Fock limit.[1,2] We here describe calculations, which include correlation, of the geometry of the molecule N_2H^+, which has been suggested to be responsible for microwave lines at 93·174 GHz.[3,4]

Restricted Hartree-Fock (RHF) calculations of the electronic ground state of N_2H^+ were first performed using the large gaussian basis of Dunning.[5] For the nitrogen functions the (9*s*5*p*) primitive basis set was contracted to [5*s*3*p*], and the hydrogen functions were the (4*s*) primitive set contracted to [3*s*]. In addition, nitrogen *d* and hydrogen *p* polarization functions having exponents of 0·83 and 1·1 respectively, were added. Large scale configuration interaction (CI) calculations were then performed including single and double excitations from the RHF configuration. The total number of such configurations included was 2036. The N–N and N–H bond lengths were optimized taking the molecule to be linear, both in the RHF approximation and including CI. The results of the calculation are summarized in the Table. The molecular geometry predicted by the RHF calculation yields a microwave transition energy some 5% too high. The inclusion of correlation effects increases both the N–N and N–H bond lengths, the microwave transition energy now being essentially in exact agreement with the experimental value, providing very strong support for the identification of the microwave line at 93·174 GHz as being due the molecular ion N_2H^+. These results highlight the inadequacy of RHF calculations in making such assignments. It should be remembered however, that our

TABLE. Calculated properties of N_2H^+

Computational		Bond lengths/Å			Quadrupole coupling constant/MHz[a]		Dipole moment
method	Energy/a.u.	N–N	N–H	$2B_e$/GHz	N^1	N^2	Debye[b]
RHF	−109·163339	1·065	1·023	98·2	−5·45	−1·34	3·35
CI	−109·414325	1·097	1·031	93·1	−4·70	−1·00	3·24

[a] N^1 is the terminal nitrogen atom. [b] With respect to the centre of mass.

calculation yields a value of B_e rather than B_0 which is obtained experimentally, so that agreement of the calculated transition energy with experiment to better than *ca.* 0·5 GHz is not to be expected.

The observed structure of the microwave spectrum yields a quadrupole coupling constant, $eqQ = -5{\cdot}69$ MHz. Our CI calculation gives a value of $-4{\cdot}70$ MHz for the terminal nitrogen atom, which is in reasonable agreement with the measured value. The value for the inner nitrogen is calculated to be $-1{\cdot}00$ MHz, whose contribution to the hyperfine structure is thus too small to be resolved experimentally. Rather better agreement with experiment is found for the coupling constant calculated from the RHF wavefunction (Table).

Thus, although the interstellar lines at 93·174 GHz have been tentatively assigned previously to the molecular ion N_2H^+,[4] the calculations reported here are needed to confirm this assignment in view of the very important changes in the molecular geometry which occur upon inclusion of correlation effects.

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