

Comment on "First Measurement of the Rotational Constants for the Homonuclear Molecular Ion He_2^+ "

In a recent Letter [1], Coman *et al.* describe a technique to derive spectroscopic information on the structure of the parent ion, using information on slow atoms emerging from a dissociative recombination process. This form of translational energy spectroscopy was used to experimentally determine the rotational constant in the electronic ground state of the He_2^+ ion. Neutral atoms are formed in dissociative recombination of the ion with low energy electrons in a plasma discharge. As a consequence of accidental near degeneracies between molecular ion energies and the internal energy of the neutral He atom in the $(1s3s)$ state, the fragment atoms are very slow. Their kinetic energy can therefore be determined with high accuracy.

The analysis of the experimental data seems to be flawed in a fundamental way. In Table I of Ref. [1] experimental entries for energy levels are displayed showing a linear progression as a function of $J(J + 1)$, which is indicative of a rotational progression. In a diatomic species, consisting of two indistinguishable spin-0 particles, the symmetrization postulate of quantum mechanics forbids the existence of quantum states with a certain parity. It is easily proven (see, e.g., Ref. [2]) that for a $^2\Sigma_u^+$ state only levels of negative parity can exist, where the parity operator is the inversion in a space-fixed frame I_{SF} or the reflection in a plane σ_v in a body-fixed frame of the molecule. Hence quantum levels with an even number of rotational angular momentum (here defined with N) do not exist for the $X^2\Sigma_u^+$ electronic ground state of the He_2^+ ion. The fact that in a state of doublet character a spin-rotation interaction $\vec{N} \cdot \vec{S}$ splits the level into two nearly degenerate components ($J = N + 1/2$ and $J = N - 1/2$) does not alter the argument. Here \vec{S} is the spin of the unpaired electron.

No violations of this symmetry postulate have been detected so far. Predictions on possible small violations of this postulate have led to experimental tests searching for very weak occurrences of forbidden lines in the spectrum of $^{16}\text{O}_2$, also consisting of two indistinguishable spin-0 particles. These studies have produced negative results at the 10^{-6} – 10^{-7} sensitivity level [3–5].

The effect of nuclear spin on the populations of rotational levels was observed in an experiment on the photodissociation of H_2^+ , also in combination with high-resolution translational spectroscopy [6]. The characteristic 3:1 ortho-para ratio was clearly obtained. Lewis *et al.* [7] analyzed the spectrum in excitation to the $f^1\Sigma_u^+$ state of $^{16}\text{O}_2$, in which half of the rotational levels were shown to be missing due to the restriction of the symmetrization postulate. Except for the singlet spin structure the symmetry of that state is the same as that of the ground state of the $^4\text{He}_2^+$ ion. In conclusion we comment that the results of the experiment on He_2^+ would have to be reinterpreted without invoking the existence of quantum states of even rotational angular momentum.

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