Comment on "Microwave Spectroscopy of High-*L* H_2 Rydberg States: The (0,1) 10 *G*, *H*, *I*, and *K* States"

In a recent Letter Sturrus *et al.*[1] have found the electric quadrupole moment of the (0,1) state of $H_2{}^+$ to be $1.6432(2)ea_0^2$ which is 0.04% larger than the calculated values to which they refer.[2] This difference is completely accounted for by the neglect of nonadiabatic corrections.

The total electric quadrupole moment is composed of a nuclear (q_n) and an electronic (q_e) part and with the origin at the nuclear center of mass it can be written as

$$Q = q_n + q_e = \tfrac{1}{2}\langle R^2\rangle - \tfrac{1}{2}[3\langle z^2\rangle - \langle r^2\rangle]\,, \qquad (1)$$

where $\langle\,\rangle$ indicates an expectation value over the complete electronic-vibrational-rotational wave function of $H_2{}^+$; R is the internuclear separation, r is the distance of the electron from the nuclear midpoint, and z is the electronic coordinate along the nuclear axis. The wave functions used in Eq. (1) may be obtained by one of three procedures: (a) the Born-Oppenheimer approximation and the use of an uncorrected potential-energy curve, (b) the Born-Oppenheimer approximation and use of a potential curve corrected by diagonal nuclear terms (adiabatic results), (c) no Born-Oppenheimer approximation but use of eigenfunctions of the complete three-particle Hamiltonian (nonadiabatic procedure). The values of Q referred to in Ref. 1 were obtained by procedure (b).

In Table I, I give results (previously reported[3] but with fewer significant figures) for Q and its components as obtained by these three procedures for the ground state ($v=0, J=0$) of $H_2{}^+$. The nonadiabatic corrections to the results of Ref. 2 are the difference between the last two columns and hence the correction to Q in its (0,0) state is $+0.0007072ea_0^2$. It is unlikely that this *correction* will be very different for the (0,1) state for which the adiabatic value of Q is $1.6425656ea_0^2$. I, therefore, estimate the nonadiabatic value of Q for the (0,1) state to be $1.64327ea_0^2$. However, before comparing this value with the experimental value, consideration should be given to relativistic corrections. This can only be done approximately. For $R=2a_0$, Sundholm, Pyykkö, and Laaksonen[4] have found that $\Delta q_e(\text{rel}) = -5.22\times10^{-6}$ and since[5] $\Delta R(\text{rel}) = -37.6\times10^{-6}$, results $\Delta q_n(\text{rel}) \cong -75.1\times10^{-6}$. So that for the fixed nuclear distance $R=2.0a_0$ the relativistic correction to Q will be of the order of $-8\times10^{-5}ea_0^2$. Assuming this is approximately the same when averaged over the (0,1) vibrational-rotational wave function, we obtain a final value of Q of $1.64319ea_0^2$, which is in extraordinarily good agreement with the experimental value.

TABLE I. Values (in atomic units, ea_0^2) for Q and its components for $H_2{}^+$ in its ground state.

	Born-Oppenheimer	Adiabatic	Nonadiabatic
$\langle z^2\rangle$	1.171 6684	1.172 1042	1.171 7374
$\langle r^2\rangle$	2.479 4673	1.480 1243	2.480 4737
$\langle R^2\rangle$	4.311 0626	4.313 3133	4.313 2779
Q	1.637 7624	1.638 5625	1.639 2697

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