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Accurate Calculation of the Infrared Spectra of HD^+, HT^+, and DT^+

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Certain transition frequencies in the vibrational-rotational spectra of HD^+, HT^+, and DT^+ have been calculated to a high degree of accuracy. For HD^+ the differences between the calculated frequencies and the recently reported observed frequencies are less than those previously obtained and are within the error bounds of the computation.

Recently Wing *et al.*[1] have reported the first *direct* measurement of the infrared vibrational-rotational spectrum of HD^+. They obtained transition frequencies to an accuracy of ± 0.002 cm^{-1} and they compared their results with certain theoretical values calculated[2] in 1967; the differences were greater than 0.04 cm^{-1}. The calculations used old values of the fundamental constants and included no relativistic or radiative corrections and only part of the nonadiabatic correction.

This Letter reports some more recent calculations for HD^+, as well as for HT^+ and DT^+ (which may be investigated experimentally in the near future[3]). The mass ratios used were $m_e/m_p = 0.000\,544\,617$, $m_e/m_d = 0.000\,272\,444$; and $m_e/m_t = 0.000\,181\,920$; and $R_\infty = 109\,737.318$ cm^{-1} was used to convert Hartree energies to inverse centimeters; these were all taken from Cohen and Taylor.[4] An adiabatic calculation was made in the same manner as described by Bishop and Wetmore,[5] using 129 points on an adiabatic potential energy curve, at internuclear distances of

TABLE I. (1,0)-(0,0) transition frequencies (cm^{-1}).

	HD^+	HT^+	DT^+
Adiabatic frequency	1913.121	1809.345	1445.440
Nonadiabatic correction	−0.140	−0.136	−0.053
Relativistic correction	0.031	0.030	0.027
Radiative correction	−0.006	−0.005	−0.004
Total transition frequency	1913.005	1809.234	1445.410

TABLE II. (1,0)-(0,1) and (1,1)-(0,2) total transition frequencies (cm^{-1}).

	HD$^+$	HT$^+$	DT$^+$
(1,0)-(0,1)	1869.142	1770.172	1420.857
(1,1)-(0,2)	1823.538	1729.635	1395.547

TABLE III. Total dissociation energies (cm^{-1}).

HD$^+ \rightarrow$ H$^+$ + D	21 516.11
HT$^+ \rightarrow$ H$^+$ + T	21 567.23
DT$^+ \rightarrow$ D$^+$ + T	21 776.74

0.2(0.1)1.6(0.025)2.6(0.1)10.0 bohrs, and a fifty-term Morse eigenfunction basis. This calculation was repeated twice: once with relativistic corrections, taken from Luke *et al.*,[6] added to the curve and once with radiative corrections, taken from Gersten,[7] added to the curve. Nonadiabatic calculations were performed for the lowest two nonrotational states in the same way as was done previously[8] for HD$^+$, i.e., a 184-term basis set of functions involving both nuclear and electronic coordinates. The nonlinear parameter γ was changed to 3.45 and 3.8 for HT$^+$ and DT$^+$, respectively; the other nonlinear parameters were taken as those for HD$^+$ shown in Table 7 of Ref. 8.

Using the notation (v,N)-(v',N') for a transition, Table I gives the values obtained for the lowest nonrotational transitions (1,0)-(0,0) and their component parts. Table II gives the total transition frequencies [including the appropriate relativistic and radiative corrections but with the nonadiabatic corrections of the (1,0)-(0,0) transitions] for (1,0)-(0,1) and (1,1)-(0,2). For HD$^+$ the values of 1869.142 and 1823.538 cm^{-1} may be compared with the experimental ones[1] of 1869.134 and 1823.533 cm^{-1}. The agreement between experiment and theory is much more satisfactory than before.[1]

Though in Table I all the components of the transition frequencies are displayed, the final numbers (bottom line) were obtained by combining the nonadiabatic frequencies (rather than the adiabatic frequencies plus nonadiabatic corrections) with the relativistic and radiative corrections; hence inaccuracies in the adiabatic frequencies are not relevant to the final numbers in this table.

There are three probable sources of error in the theoretical values in Table II: inaccurate nonadiabatic energies (errors of possibly 0.004 cm^{-1} on a level and therefore 0.008 cm^{-1} on a transition; this includes errors in the adiabatic component), inaccurate relativistic corrections (Luke *et al.* give only three significant figures for the correction as a function of internuclear distance and there is a possible rounding-off error of 0.005 cm^{-1} and a 0.01 cm^{-1} error on a transition), and the use of *rotationless* nonadiabatic corrections for transitions involving rotational states (though this error is likely to be only of the order of 0.001 cm^{-1}).

The errors given above are upper limits; nonetheless they are an order of magnitude greater than the experimental error limits. It is unlikely that there will be much improvement in the near future in the accuracy of the nonadiabatic part of the calculation, though it would be possible to recalculate the relativistic component to more significant figures and reduce the error there. Finally, attention is drawn to the fact that only the lowest two nonadiabatic energies have been calculated for these species; extension to higher states, requiring an expanded basis set, would seem to be worthwhile since (a) it would give further data for comparison with Wing *et al.*'s results and (b) the higher transition frequencies are more dependent on the nuclear masses used and might thereby allow them to be refined as was speculated by Wing *et al.*

Dissociation energies (including nonadiabatic, relativistic, and radiative effects) are given in Table III for the three species.

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