Hyperfine Structure in the Infrared Spectrum of ^{3}He ^{4}He$^+$

Nan Yu [a]

Department of Physics, University of Arizona, Tucson, Arizona 85721

William H. Wing

Department of Physics and Optical Sciences Center, University of Arizona, Tucson, Arizona, 85721

Ludwik Adamowicz

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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In our recent experiment, the hyperfine splittings of ^{3}He ^{4}He$^+$ were observed in the infrared spectrum. Now we present an *ab initio* quantum-mechanical calculation of hyperfine structure in the (1-0) vibrational band of the ^{3}He ^{4}He$^+$ ground electronic state. The hyperfine interaction coefficients b, c, and γ are calculated by using the numerical multiconfiguration self-consistent-field method at a set of closely spaced internuclear distances and then averaged over nuclear coordinates for individual vibration-rotation states. The theoretical spectra agree well with the experimental observations.

Since the advent of microwave spectroscopy and other high-precision spectroscopic methods, the study of the hyperfine structure of molecules has been an important part of molecular structure investigation. Astrophysical observation of many interstellar molecules such as CH and OH relies largely on the detection of radio-frequency hyperfine transitions. Hyperfine interaction coefficients, especially the Fermi contact term, which is directly proportional to the electron-spin density at the nucleus, are very sensitive to the molecular structure. Thus a comparison of theoretical hyperfine spectra with experimental ones provides a stringent test for the theoretical models and promotes the convergence of theoretical and experimental quantum chemistry into a unified discipline. Despite many available high-precision experimental hyperfine data, *ab initio* studies are rather scarce. To our knowledge, only the hyperfine structures of H_2^+ and HD$^+$ have been treated theoretically in great detail from first principles.[1,2] Calculations for other diatomic molecules are very limited at present. Recently, extensive configuration-interaction studies have been performed for a few diatomic molecules but the calculations have been limited to the equilibrium bond lengths only.[3] Calculations that are specific to vibration-rotation states[4] are even fewer.

In our recent Doppler-tuned ion-beam laser-resonance experiment,[5] the infrared vibration-rotation transitions of ^{3}He ^{4}He$^+$ were observed. The resonance traces showed multipeak structures, which were believed to result from the magnetic hyperfine interaction. ^{3}He ^{4}He$^+$ is one of the simplest multielectron open-shell molecules and is therefore especially amenable to detailed *ab initio* study. In this Letter, we present the first *ab initio* calculation of the hyperfine structure of ^{3}He ^{4}He$^+$ using the numerical multiconfiguration self-consistent-field (MCSCF) method[6] within the Born-Oppenheimer approximation. The spectral splittings predicted by the calculation agree well with the experimental observations.

The effective hyperfine interaction Hamiltonian for ^{3}He ^{4}He$^+$ with the internuclear distance R as a parameter can be written

$$H_{\text{eff}}(R) = b(R)\mathbf{S}\cdot\mathbf{I} + c(R)S_z I_z + \gamma(R)\mathbf{S}\cdot\mathbf{N}, \qquad (1)$$

where $\mathbf{S}$, $\mathbf{I}$, and $\mathbf{N}$ are, respectively, the total electronic spin, the nuclear spin of ^{3}He, and the angular momentum of the molecular rotation in units of $\hbar$. The hyperfine interaction coefficients $b(R)$, $c(R)$, and $\gamma(R)$ are averages over the electron coordinates of the ground electronic state as discussed below. The nuclear-spin–rotation interaction is believed to be a much smaller effect and therefore has been omitted from the effective Hamiltonian.

The explicit expressions for b and c, first derived by Frosh and Foley,[7] can be written

$$b(R) = g_e g_n \mu_0 \mu_n \left[\frac{8\pi}{3}\langle\delta(\mathbf{r})\rangle_{\text{sav}} + \left\langle \frac{x^2-z^2}{r^5} \right\rangle_{\text{sav}} \right], \qquad (2a)$$

$$c(R) = g_e g_n \mu_0 \mu_n \left\langle -3\frac{x^2-z^2}{r^5} \right\rangle_{\text{sav}}, \qquad (2b)$$

where $\mathbf{r}$ is the unpaired electron position vector relative to the center of ^{3}He and the other constants have their usual meanings. $\langle\ \rangle_{\text{sav}}$ denotes the electron spin- and coordinate-averaged expectation value for the open-shell ^{3}He ^{4}He$^+$ electronic ground state $(1\sigma_g^2 1\sigma_u)^2\Sigma_u$ calculated at the internuclear distance R. The first term in $b(R)$ is the well-known Fermi-contact term. The second term in $b(R)$ and $c(R)$ constitutes the dipole-dipole interaction.

The first-order spin-rotation interaction has been discussed by Veseth.[8] The electron part of the spin-rotation term involves two-electron parameters and is complicated to compute. Therefore, we will make an approxima-

tion that the contribution from core electrons is effectively taken into account by reducing the nuclear charge, which enters the expression for $\gamma(R)$, from $Z=2$ to $Z_{eff}=1$. Then the first-order spin-rotation interaction takes the form

$$\gamma(R) = 2Z_{eff} g_e \mu_0 \mu_n \left[\frac{m_p}{m_r} \right] \frac{1}{R} \left\langle \frac{z}{r^3} \right\rangle_{sav}, \qquad (2c)$$

where m_p is the proton mass and m_r is the nuclear reduced mass.

Usually there is an important second-order contribution to the spin-rotation term. It accounts for the additional interaction between the electron spin and the electronic orbital angular momentum induced by the molecular rotation. The calculation of the second-order term is rather involved even for the simplest isotopes of the H_2^+ molecule.[2] According to the usual second-order perturbation theory, the contribution is expected to be small for a light element with a small spin-orbit coupling constant when the lowest Π state is positioned far away from the Σ ground state. In the case of H_2^+,[2] the second-order term has been calculated to be only about one-tenth of the first-order term. We believe that the second-order term for the ground state of $^3He\,^4He^+$ will be no more important, and probably will be less so, because its lowest Π state is even farther away than is that of H_2^+. In addition, our present experimental data are relatively insensitive to γ. Accordingly, we have omitted the second-order interaction.

The electronic wave function is generated with use of the numerical MCSCF procedure.[6] The numerical molecular orbitals in this method, which is limited to one- and two-center systems in its present implementation, are represented as partial-wave expansions in elliptical coordinates with numerical radial components. In the usual MCSCF approaches, orbitals are represented by truncated analytic basis-set expansions. The errors induced by the truncation can be serious if an improper basis set is chosen. The numerical MCSCF method avoids this deficiency by solving the Fock equations numerically on a densely spaced grid of points. The resulting molecular orbitals are essentially exact for a given configuration list because the monotonic convergence property of the partial-wave expansion gives the analyst control over computational errors. The most important advantage numerical MCSCF orbitals have for calculating hyperfine structure coefficients is their uniformly good quality at nuclei as well as elsewhere.

The numerical computation was initiated with a single-configuration wave function near the equilibrium internuclear distance R_e. Then lists of 5, 6, 12, 18, 24, 31, and 48 configurations were selected, based on our previous computational experience with open-shell anions, to account for the most important electron correlation effects in He_2^+. Attention also was paid to the modeling of nuances of the electron-spin-density distribution near nuclei. Considered were correlation of the $1\sigma_g$ core electrons, pair correlation between the core electrons and the $1\sigma_u$ electron, simultaneous correlation of all three electrons, and spin polarization of the core by the $1\sigma_u$ electron. Preliminary computations near R_e showed that the 31- and 48-configuration sets gave detectable but insignificant differences in the hyperfine coefficients b, c, and γ, while major changes occurred only below 18 configurations. However, the 18-configuration set gave significantly higher electronic energies at selected values of R. Local properties such as hyperfine parameters tend to be more sensitive to fine wave-function details than do global properties such as energy. Convergence of the $1\sigma_u$ orbital near the nuclei is particularly important in our case, since it affects the spin averaging the most. Accordingly, we chose the 31-configuration set, the largest affordable, for final computations at 25 internuclear distances from 1.3 to 4.6 bohrs. Resulting potential energies and hyperfine coefficients[9] are listed in Table I.

For the final calculations, we required that the $1\sigma_u$ orbital satisfy the cusp condition $\partial \ln\psi/\partial r + Z = 0$ [atomic units, $\psi(0)\neq 0$] to within 10^{-4} at each nucleus. The to-

TABLE I. The numerical MCSCF Born-Oppenheimer potential energy and electronic hyperfine coefficients for $^3He\,^4He^+$ from the 31-configuration calculation. For accuracy considerations, see text.

R (bohr)	Energy (hartree)	−b(R) (MHz)	−c(R) (MHz)	−γ(R) (MHz)
1.3	−4.84388695	4424.54	47.43	20.69
1.4	−4.89292292	4611.88	32.45	16.51
1.511781	−4.93157910	4752.92	21.30	12.76
1.6	−4.95289342	4827.43	15.55	10.37
1.700753	−4.96967920	4880.30	11.00	8.172
1.79524	−4.97976143	4908.90	8.249	6.527
1.85	−4.98362588	4918.10	7.109	5.731
1.9	−4.98611111	4922.53	6.280	5.087
1.92	−4.98686194	4923.00	5.988	4.848
1.94	−4.98747591	4923.97	5.747	4.624
1.95	−4.98774018	4923.40	5.600	4.520
2.0	−4.98861283	4922.38	5.099	4.006
2.049627	−4.98888532	4919.20	4.715	3.557
2.1	−4.98859585	4914.91	4.435	3.152
2.2	−4.98676331	4902.59	4.109	2.472
2.35	−4.98171952	4877.28	3.929	1.705
2.45	−4.97742159	4858.85	3.949	1.319
2.6	−4.97023292	4826.07	4.001	0.8754
2.834467	−4.95860809	4775.62	4.168	0.4078
3.306878	−4.93789894	4678.14	4.468	−0.06738
3.55	−4.92951126	4633.58	4.518	−0.1836
3.8	−4.92249428	4591.00	4.478	−0.2538
4.05	−4.91693188	4553.58	4.360	−0.2912
4.3	−4.91259580	4521.09	4.181	−0.3066
4.6	−4.90869271	4488.56	3.909	−0.3065

tal electronic energy convergence limit was set at 2.5×10^{-7} hartree. Computation continued at each value of R until both conditions were satisfied. The former was much stricter than the latter, except at large R, where the energy condition became harder to satisfy. Our potential energies are about 10×10^{-7} hartree higher than those from the extensive calculations by Khan and Jordan,[10] who used a large fixed analytic basis set. Our hyperfine coefficients remained stable to the numbers of digits quoted in Table I for the last few numerical MCSCF iterations. Presumably results would not have differed importantly if a somewhat smaller configuration list had been used. List details and the effects of changes are reported more fully elsewhere.[11]

The spectroscopic constants b, c, and γ for individual vibration-rotation states are expectation values of $b(R)$, $c(R)$, and $\gamma(R)$, averaged over nuclear coordinates. The values of R used in Table I are sufficient for accurate averaging in the first two vibrational states. Table II contains these results. Evidently the variation of b between vibrational states is not only substantial but is larger than the values of c and γ. Indeed, as we shall see, it is primarily the vibrational variation of b that has been experimentally observed.

Because the ground state of $^4\text{He}\,^3\text{He}^+$ is a Σ state, the electron spin-orbit interaction vanishes. The spin $\mathbf{S}$ is quantized in laboratory-fixed space with strong coupling to the nuclear spin. The angular momentum coupling scheme then approximates closely Hund's case $(b_{\beta S})$ in which $\mathbf{G} = \mathbf{I} + \mathbf{S}$ and $\mathbf{F} = \mathbf{G} + \mathbf{N}$. A suitable basis for this coupling scheme is $|\,(SI)G,N,F\rangle$, because it renders the $\mathbf{S} \cdot \mathbf{I}$ term diagonal. The off-diagonal hyperfine Hamiltonian matrix elements are then very small. At the present accuracy of the experiment, total diagonalization of the hyperfine Hamiltonian is unnecessary. Therefore

we used only the diagonal terms in reconstructing the hyperfine spectrum. This is the cause of a slight apparent violation of the center-of-gravity theorem in our results.

To simulate the observed spectrum, relative line intensities were computed from electric-dipole vibration-rotation hyperfine matrix elements and degeneracy factors. In our experimental situation, the homogeneous (transit-broadened) width of the transitions may be partially saturated, although the much larger inhomogeneous (velocity-distribution-broadened) width is unsaturated. In this domain, the use of unsaturated transition strengths is an adequate approximation. The results show no "spin-flipping" transitions because of the weak magnetic interaction with the infrared laser field. For not too small rotational quantum number N, transitions with $\Delta F = \Delta N$ are the strongest, while others are much weaker. The hyperfine energy levels of the vibration-rotation states $(1,7)$ and $(0,6)$, and the allowed transitions with their relative intensities, are pictured in Fig. 1. A theoretical spectrum, obtained by assigning each transition a Gaussian line shape having the estimated experimental linewidth of 6 MHz, is also shown. Transitions other than those having $\Delta F = \Delta N$ are too weak to register on the scale used, and have been omitted. The theoretical spectrum very closely resembles the experimental spectrum, which was first published in Ref. 5. The strongest transitions of the $\Delta F = \Delta N$ set all have approximately the same transition strength. But the transitions of the $G = 1$ triplet are separated by only about 1 MHz, and hence are not resolved by the current experiment. Other transitions are too weak to be seen. Therefore, the spectrum exhibits two resolved peaks with an apparent intensity ratio of 3 to 1.

Several experimental factors contribute to the observed line shape, which is neither Gaussian nor Lorentzian and is slightly asymmetric. The relatively low signal-to-noise ratios of the resonance traces preclude a full analysis including all physical effects. To estimate the sensitivity of the results to the line-shape model, we fitted a test resonance trace with several modified Gaussian functions containing adjustable asymmetry parameters; the peak splittings, however, varied insignificantly. Consequently, we finally fitted each resolved peak of each resonance trace with a standard Gaussian whose height, width, and center position was independently adjusted. For the $(1,7)-(0,6)$ line, the fitted separation of the two dominant peaks is 17.7 MHz. The standard fitting error of the line centers is less than 0.5 MHz. Our theory predicts a peak separation of 17.0 MHz, which is in good (1.4 standard deviation) agreement with the experiment.

It is interesting to point out that the single-configuration computation, extended to the entire set of internuclear distances and vibrationally averaged, predicts a separation of 26 MHz, indicating that electron correlation has a significant effect on hyperfine coef-
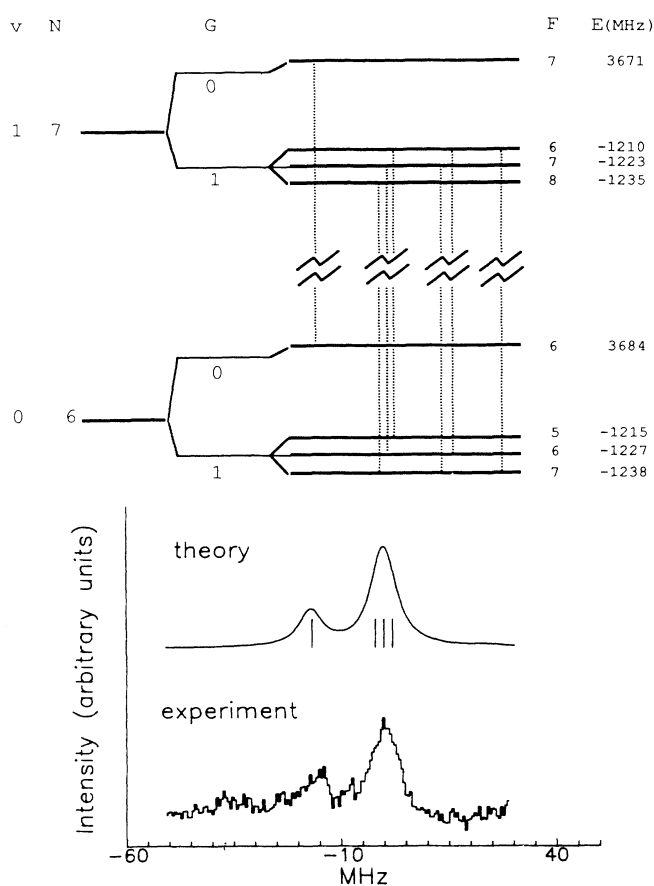
TABLE II. The $^3\text{He}\,^4\text{He}^+$ hyperfine constants for the first two vibrational states, in MHz. For accuracy considerations, see text.

N	-b		-c		-γ	
	v=0	v=1	v=0	v=1	v=0	v=1
0	4911.28	4894.36	4.894	5.185	3.494	3.333
1	4911.28	4894.32	4.892	5.182	3.491	3.330
2	4911.21	4894.26	4.887	5.177	3.485	3.325
3	4911.11	4894.16	4.880	5.170	3.477	3.316
4	4911.01	4894.06	4.878	5.160	3.465	3.305
5	4910.88	4893.89	4.859	5.148	3.450	3.291
6	4910.71	4893.69	4.846	5.134	3.433	3.274
7	4910.51	4893.46	4.830	5.117	3.413	3.254
8	4910.25	4893.23	4.812	5.098	3.390	3.232
9	4909.98	4892.93	4.793	5.077	3.364	3.207
10	4909.68	4892.56	4.771	5.054	3.336	3.180
11	4909.32	4892.20	4.748	5.029	3.305	3.150
12	4908.95	4891.76	4.724	5.003	3.272	3.117

FIG. 1. The hyperfine levels of the vibration-rotation states (1,7) and (0,6) are shown (not to scale) in the upper half of the figure. Energies E are given relative to that of the vibration-rotation state. The reconstructed theoretical spectrum and the experimental spectrum of the transitions between the two states are shown in the lower half of the figure. The allowed transitions and their relative intensities (see text) are also shown. The intensities of some transitions are too low to register on the theoretical spectrum plot.

ficients even for a three-electron molecule. How much of the effect arises from hyperfine parameter changes and how much from changes in the potential-energy surface and vibrational wave functions remains to be determined.

To our knowledge, our work is the first *ab initio* calculation of the hyperfine structure of a multielectron open-shell diatomic molecule which uses an extended MCSCF wave function and includes vibration-rotation averaging. Our twofold objective has been to calculate the ^{3}He ^{4}He$^+$ hyperfine spectrum to present experimental accuracy and to lay a consistent basis for improved calculations in this and similar molecules. The first part has been achieved. Within the approximations noted, we believe the second has also. Propagating errors within our model suggests that the overall fractional computational errors of b and c are at most about equal to the

cusp condition error limit, or 10^{-4}. However, model errors, notably the Born-Oppenheimer approximation, limit the absolute fractional accuracy of other MCSCF spectroscopic quantities for ^{3}He ^{4}He$^+$ to about 1 part in 10^3 at present.[5] This is a more realistic error estimate for b and c as well. The experiment can be considered to have verified the vibrational variation of b to within about 3%. γ is probably less accurate because of its further approximations; improvement would require actual evaluation of the effects we have subsumed into the approximation $Z_{\text{eff}} = 1$ in the first-order term, and also evaluation of the second-order term. The effort to remove these limitations and the minor benign simplifications we have made, and to calculate other small Hamiltonian terms, will be warranted once a fully resolved hyperfine spectrum of ^{3}He ^{4}He$^+$ becomes available.

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[a]Present address: Department of Physics, University of Washington, Seattle, WA 98195.

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