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"Vibrational" and "Rotational" Energy Levels as Protonic Structure in Molecules*

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The "vibrational" structure is shown to consist of electric dipole transitions of the protons from their ground state characterized by a principal quantum number n, to an excited state with $n' = n+1$. In hydrogen fluoride, the transition from the ground state 108s to the state 109p is calculated to be 4277.4 cm^{-1} which compares well with the experimental transition of 3961.57 cm^{-1}. For lithium hydride in its first excited electronic state, an energy of 1562.3 cm^{-1} is calculated for the first protonic transition. The experimental value is 1359.2 cm^{-1}. Water, ammonia, and methane are also discussed, as are the electric quadrupole, magnetic dipole, the two-proton, and the electron-proton transitions. It is postulated that the "rotational" structure arises from electric dipole transitions from the ground state to states of higher angular momentum with the same principal quantum number as the ground state.

I. INTRODUCTION

In several papers we have discussed the protonic structure of molecules.[1-3] Among the many objections that have been made against the concept, one has been the absence of the structure usually attributed to vibrations and rotations of the nuclear framework in the calculated protonic spectra. In this paper we will show how that structure arises without using vibrations or rotations.

II. "VIBRATIONAL" STRUCTURE

We will make some drastic approximations to the Hamiltonian for hydrogen fluoride given by Eq. (7) in Ref. 3. The approximations are not required to solve Schrödinger's equation, but they do make much clearer what we wish to show here. The Hamiltonian for hydrogen fluoride will be approximated by

$$H = -(\hbar^2/2\mu)\nabla^2 - (Ze^2/r) \; , \tag{1}$$

where $\mu = m_p m_f/(m_p + m_f)$, m_p and m_f are the protonic mass and the mass of the fluorine nucleus, respectively, and r is the distance of the proton from the fluorine nucleus. Schrödinger's equation becomes

$$H\phi \approx \left(E - E' + \sum_i \frac{e^2}{r_{ip}}\right)\phi = -\epsilon\phi \; , \tag{2}$$

where E' is approximately the energy of the negative fluoride ion and the r_{ip} are the electron-to-proton distances. [This approximation is not as drastic as the usual one, where Eq. (1) is used but with $1/r$ replaced by r^2.] The parameter Z is an effective charge. We know the solution of Eq. (2). The radial part of the wave function is

$$R_{nl}(r) = N\rho^l e^{-Zr/nA_0} L_{n+l}^{2l+1}(\rho) \; , \tag{3}$$

where N is the normalization constant and L is the Laguerre polynomial, and

$$\rho = (2Z/nA_0)r \; ,$$

where

$$A_0 = \frac{\hbar^2}{\mu e^2} = 0.303\,494 \times 10^{-11}\ \text{cm}$$

$$= 0.573\,532 \times 10^{-3}\ \text{bohr}. \tag{4}$$

The energy levels are

$$\epsilon_n = Z^2 e^2/2n^2 A_0 \; . \tag{5}$$

We solved variationally Schrödinger's equation with an exact spin-free and nonrelativistic Hamiltonian for HF using a function of the form $r^{n-1}e^{-\zeta r}$ for the proton. We found that $n = 108$ and $\zeta = 61$ minimized the energy. Let

$$\zeta = Z/nA_0 \tag{6}$$

and

$$R_{nl} \approx N r^{n-1} e^{-\zeta r}.$$

When we substitute the above values of n, ζ, and A_0 (in bohrs) into Eq. (6) and solve for Z, we get

$Z = 3.77843$. Note that what we have done is to require that the proton be mostly at $r = (n-1)/\zeta$. If this were not done, the proton would see a repulsive potential rather than an attractive potential long before it got to A_0. (If, in fact, we were describing an antiproton-proton atom, the distance at which one would predict that he would most likely find a proton or an antiproton would be at 0.576408×10^{-11} cm). With the above choice of Z, we get

$$\epsilon_{108} = 1.067057 \text{ hartrees}$$

and

$$\epsilon_{109} = 1.047568 \text{ hartrees},$$

$$\epsilon_{108} - \epsilon_{109} = 0.019489 \text{ hartrees} = 4277.4 \text{ cm}^{-1} .$$

The first "vibrational" transition in HF is 3961.57 cm^{-1}. Our error is 315.8 cm^{-1} or less than 10%. The next experimental transition is 7751.86 cm^{-1}. This would correspond to $\epsilon_{108} - \epsilon_{110} = 8330.0 \text{ cm}^{-1}$. The third experimental transition is 11 276.72 cm^{-1}, which would correspond to $\epsilon_{108} - \epsilon_{111} = 12879.8 \text{ cm}^{-1}$. Our agreement is getting worse, as it should; because the maximum of the function has changed from 1.75 to 1.80 bohr, both E' and $\sum_i e^2/r_{ip}$ should change, but we have assumed them to be constant. These transitions are allowed by the electric dipole operator.[4] Therefore, they will be restricted by the selection rules $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$. In addition to these transitions, the electric quadrupole operator[4] allows transitions with the selection rules $\Delta l = 0, \pm 2$ and $\Delta m = 0 \pm 1, \pm 2$. These will be much weaker, though. Even weaker than these are those transitions allowed by the magnetic dipole operator[4] whose selection rules are $\Delta l = 0$ and $\Delta m = 0, \pm 1$. Finally there will be transitions where an electron and a proton are simultaneously excited, each restricted by the electric dipole selection rules. These will be weaker than the electric quadrupole but stronger than the magnetic dipole transitions.

We also have a wave function for LiH in its first excited electronic state (the electronic part of the wave function was $1s^2\, 2s\, 2p$) for which we found an $n = 125$ and $\zeta = 38$. The A_0 is 0.623593×10^{-3} bohr. From these we get a $Z = 2.96207$ and

$$\epsilon_{125} - \epsilon_{126} = 1562.3 \text{ cm}^{-1} .$$

The experimental value is 1359.2 cm^{-1}.

Since we have been successful with the two monohydrides, we should consider the other hydrides for which we have wave functions. These are water, ammonia, and methane.[3] We found a ^3P ground state in an sp configuration for water. There is an allowed transition to the ^3P of the p^2 configuration but the energy difference of about 0.07 hartrees between these states is much too large to be of the kind we are looking for. There will certainly be a close-lying ^3P of some p^2 configuration whose n is less than the ground state n. However, there can be no electric dipole transition to this state. This can be seen as follows. Let the ground-state wave function be

$$\psi_n = 2^{-1/2} \det |s(1) p_1(2)|$$

and the excited state

$$\psi_{n'} = 2^{-1/2} \det |p_0'(1) p_1'(2)| ,$$

where the primed function represents a function with n different from the unprimed function, and $\int p_1 p_1' \, dr = 0$. For light polarized in the z direction, the transition integral is proportional to

$$\int \psi_n (z_1 + z_2) \psi_{n'} \, dr_1 dr_2 = \int s z p_0' \, dr_1 \int p_1 p_1' \, dr_2 ,$$

but $\int p_1 p_1' \, dr = 0$. The argument here is weak because it depends on an orbital description. Now let the excited state be

$$\psi_{n'} = (\tfrac{1}{2})[\det |p_0'(1) p_1(2)| - \det |p_1'(1) p_0(2)|] ,$$

where p' represents $n'p$ and $n' = n + 1$. Then

$$\int \psi_n (z_1 + z_2) \psi_{n'} \, dr_1 dr_2 = 2^{-1/2} \int s z p_0' \, dr .$$

Therefore, there can be transitions where a single proton is excited from its ground-state $nsnp$ configuration to an $n'pnp$ configuration. There can also be transitions to an $nsn's$ configuration. These two excited states will be different in energy because the potential seen by the proton is only approximately Coulombic. In addition to these transitions there will be a low-intensity transition to an $n'sn'p$ state allowed by the operator proportional to $x_i z_j$ where i and j refer to different protons.[4] In ammonia the transitions will be from the $nsnp^2$ ground state to an $n'pnp^2$ and an $nsn'snp$ excited state. The $x_i z_j$ operator would allow transitions to an $n'sn'pnp$ excited state. In methane the ground state is $nsnp^3$. The high-intensity transitions would be to the $np'np^2$ and $nsns'np^2$ excited states. The low-intensity transitions would be to the $n'sn'pnp^2$ state.

We note that in all of these molecules the low-intensity excited state can also be reached by the excitation of more than one proton. In water we could have $nsnp$ to $n'pnp$ to $n'pn's$, in ammonia $nsnp^2$ to $np'np^2$ to $np'ns'np$, and in methane $nsnp^3$ to $n'pnp^3$ to $n'pn'snp^2$. The electric quadrupole operator would allow transitions such as $nsnp$ to $nsnf$, $ndnp$, $n'dnp$, or $nsn'f$ in water; $nsnp^2$ to $nsnpnf$, $ndnp^2$, $n'dnp^2$, or $nsnpn'f$ in ammonia; $nsnp^3$ to $nsnp^2nf$, $ndnp^3$, $n'dnp^3$, or $nsnp^3n'f$ in methane. In addition to these there would also be the very weak magnetic dipole transitions and the transitions exciting an electron and a proton simultaneously.

If we use more boldness than logic we can use the Hamiltonian of Eq. (2) to get some idea of the energies involved in the single-proton excitations in water, ammonia, and methane. The data are

TABLE I. Predicted single-proton excitations in water, ammonia, and methane.

	n^a	ζ^a	Z	A_0(bohr $\times 10^3$)	$\epsilon_n - \epsilon_{n+1}$(cm^{-1})
H_20	115.0	63.0	4.19444	0.578943	4328.13
NH_3	125.0	63.0	4.59750	0.583809	4022.39
CH_4	125.0	57.0	4.20601	0.590324	3327.52

[a]We have rounded off the numbers given in Ref. 3.

summarized in Table I. The values are at least of the right order of magnitude and decrease as they should from water to methane. Of course, the Hamiltonian of Eq. (2) is much worse for these molecules than for the monohydrides.

One obvious use of the analysis of "vibrational" structure presented here is to give some rough idea of a good first choice of n's and ζ's for calculations. We require that $(n-1)/\zeta = R$, or

$$\zeta = (n-1)/R \; , \tag{7}$$

where R is the experimentally determined maximum in the wave function of the nucleus (i.e., the bond length). From Eqs. (6) and (7), we get $Z = n(n-1) \times A_0/R$. Then

$$\epsilon_n - \epsilon_{n+1} = \frac{[n(n-1)A_0/R]^2}{2A_0}\left(\frac{1}{n^2} \quad \frac{1}{(n+1)^2}\right) \approx \frac{nA_0}{R^2} \; ,$$

or

$$n \approx (\epsilon_n - \epsilon_{n+1})R^2/A_0$$

for large n. If we try this for HF we find $n \approx 94.0$ and $\zeta \approx 54.4$. For InCl, for which $A_0 \approx 0.21 \times 10^{-4}$ bohr, $R \approx 4.5$ bohr, and $\Delta\epsilon \approx 9 \times 10^{-4}$ hartrees, we would expect $n \approx 913$ and $\zeta \approx 203$. For a molecule such as CO, the e^2 in the potential term of the Hamiltonian of Eq. (2) would have to be changed to q^2 where $q = 2e$, then $A_0 = 1/(4\mu) \approx 0.20 \times 10^{-4}$ bohr, $R \approx 2.1$ bohr, and $\Delta\epsilon \approx 9.0 \times 10^{-3}$ hartrees, and $n \approx 79$ and $\zeta \approx 38$.

III. "ROTATIONAL" STRUCTURE

We have said already that the energies of the protons do not depend only on n. Different values of l for the same n will give different energy levels. These changes in l are, in fact, the "rotational" structure. In other words the "rotational" structure consists of transitions allowed by the electric dipole operator from the ground-state configuration to higher angular momentum states. In HF, the ground state for the proton is $n = 108$, $l = 0$, $m = 0$. The excited states would be $l = 1$, $l = 3$, $l = 5$ and so on, all with $n = 108$. In addition to these transitions there should exist very weak electric quadrupole transitions to the even l states. We should make clear that the electric dipole operator has nothing to do with a permanent dipole moment. The concept of a permanent dipole moment can have meaning only in the Born-Oppenheimer approximation. Since the dipole moment operator vanishes for homonuclear diatomic molecules,[4] they have no "rotational" or "vibrational" structure of the electric dipole type. However, the electric quadrupole operator does not vanish, so they will have structure allowed by that operator.

The "rotational" structure of the polyatomic molecules is more complicated, and our simple model Hamiltonian is not good enough to allow us to interpret these transitions.

IV. CONCLUSION

There remains much to be done. We must show why methane whose dipole moment operator does not vanish does not have "rotational" structure. We must reinterpret the concept of permanent dipole moments in terms of an external field.[5] We must investigate the effects of spin-orbit and spin-spin interactions. We must calculate wave functions for molecules such as D_2O, ND_3, CD_4, etc., which require a symmetric wave function for the deuterons for which we have already given the matrix elements of the Hamiltonian.[6] We must extend this work to nonhydrides which, as we have shown here, may not have forbiddingly high n's. (Even if they do, Gaussian functions rather than Slater functions could be used.) It should be clear, though, that it is not necessary, and it may not be desirable, to ascribe to small molecules, vibrations, rotations, hindered rotations, inversions, and so on. Molecular structure can be described simply and succinctly by using Schrödinger's equation with no approximations in the Hamiltonian. It would have been very surprising had this not been possible.

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