diagonalization of the matrix, Porter assigned the transitions provisionally and then made an adjustment of $+8.9\ \mathrm{cm}^{-1}$ in the vibrational frequencies and + 1.6% in the rotational energies to obtain the best fit of the experimental values. The close agreement ($0.03\ \mathrm{cm}^{-1}$ maximum error) on all four assigned transitions confirms the assignments, in our judgment. The remaining four transitions appear to involve higher vibrational levels, higher rotational levels, or both. Unequivocal assignment was not possible because of the high density of candidates.

This Letter reports preliminary data for a few transitions. We expect that additional resonances will be found soom. Only about 4% of the infrared spectral region presently accessible to our experimental apparatus has been explored thus far. Such additional data would greatly facilitate transition identification. We hope that these results, combined with the results of Oka,[1] will lead to precise predictions of transitions observable in the interstellar medium in H_3^+ and H_2D^+. We also plan to search for the H_2D^+ spectrum in the laboratory.

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Ab Initio Prediction of the Rotation-Vibration Spectrum of H_3^+ and D_3^+

G. D. Carney
Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

and

R. N. Porter
Department of Chemistry, State University of New York, Stony Brook, New York 11794

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The first few lines in the *P*, *Q*, and *R* branches of the rotation-vibration spectra of the equilateral-triangle molecular ions H_3^+ and D_3^+, obtained by *ab initio* nonperturbative calculations, are reported. Comparison with observations indicates an accuracy better than 1% was obtained for both the infrared-active fundamental vibration frequency and the equilibrium internuclear distances.

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In this Letter we report the first results of an *ab initio* nonperturbative calculation of the rotation-vibration spectrum of a highly anharmonic, nonrigid polyatomic molecule. Our choice of system is H_3^+ (and its deuterium analogue D_3^+), an ion thought to play an important role in the formation of molecules in the interstellar medium.[1] Although the calculations were carried out in the absence of observed spectra, during the preparation of our report of the results measurements of rotation-vibration spectra were achieved by Oka[2] for H_3^+ and by Shy *et al.*[3] for D_3^+, in two quite remarkable experiments.

The calculated spectra are sensitive to the potential-energy surface.[4] By conventional standards (size of electronic basis set, low absolute electronic eigenenergies), the best calculation of a potential-energy surface for H_3^+ is that of Dykstra *et al.*[5] However, the most convenient surface available at the time these calculations were begun was a configuration-interaction (CI) surface[6] designed to be relatively consistent over the required range of nuclear coordinates. We therefor report here our results for our CI surface and let its accuracy be assessed by comparison with the observations. Details of our use of the method of vibrational-configuration interaction to obtain the lowest pure-vibrational (i.e., $J=0$) eigenenergies have been reported.[7]

In the work reported here, we diagonalize the Born-Oppenheimer Hamiltonian for nuclear motion in the product basis of the pure-vibrational eigenfunctions and the symmetric-top eigenfunctions in real form.[8] If Q_i ($i=1,2,3$) are the normal-mode coordinates for an equilateral X_3 molecule, the Hamiltonian for bound nuclear motion[9] can be expressed as a matrix in the pure-vibrational eigenfunction basis:

$$H_{nm} = E_n s_{nm} + \tfrac{1}{2}A_{nm}J_x^{\,2} + \tfrac{1}{2}B_{nm}J_y^{\,2} + \tfrac{1}{2}C_{nm}J_z^{\,2} + \tfrac{1}{2}D_{nm}(J_xJ_y + J_yJ_x) + iF_{nm}J_z\,, \qquad (1)$$

TABLE I. Vibrational matrix for the rotational coefficients.[a]

n	m	⟨n|A|m⟩	⟨n|B|m⟩	⟨n|C|m⟩	⟨n|D|m⟩	⟨n|E|m⟩	⟨n|F|m⟩
				(H_3^+)			
1	1	86.446	86.450	41.129	0.0	0.0	0.0
2	1	-15.197	15.185	-0.007	0.096	0.0	0.0
3	1	0.096	-0.096	0.0	15.193	0.0	0.0
4	1	-12.484	-12.526	-6.223	0.0	0.0	0.0
2	2	82.735	92.638	39.470	-0.061	2515.99	0.0
3	2	0.062	-0.062	0.0	-4.846	0.0	37.031
4	2	-2.353	2.347	-0.008	0.015	0.0	0.0
3	3	92.509	82.833	39.471	0.062	2516.17	0.0
4	3	0.015	-0.015	0.0	2.360	0.0	0.051
4	4	84.308	84.384	39.984	0.0	3185.32	0.0
				(D_3^+)			
1	1	43.311	43.311	20.918	0.0	0.0	0.0
2	1	-6.417	6.415	0.0	0.066	0.0	0.0
3	1	0.066	-0.066	0.0	6.416	0.0	0.0
4	1	-5.425	-5.429	-2.701	0.0	0.0	0.0
2	2	41.939	45.353	20.308	-0.035	1826.39	0.0
3	2	0.0351	-0.0351	0.000	-1.695	0.0	19.423
4	2	-0.795	0.794	0.000	0.008	0.0	0.0
3	3	45.338	41.951	20.308	0.035	1826.42	0.0
4	3	0.008	-0.008	0.000	0.795	0.0	0.007
4	4	42.542	42.552	20.514	0.000	2307.47	0.0

[a] Values are given in cm^{-1}. The matrices A, B, and C are symmetric; the matrix F is skew symmetric; E is the diagonal matrix of the pure vibration ($J=0$) eigenenergies.

where $\vec{J}$ is the rotational angular-momentum operator whose components are referred to a molecule-fixed coordinate system with origins at the center of mass, z axis perpendicular to the molecular plane, and x axis bisecting an X-X "bond." In Eq. (1), E_n is the nth pure-vibrational eigenenergy and the rotational coefficient matrices have the general form

$$\langle n|f(Q_1,Q_2,Q_3)|m\rangle,$$

where $|m\rangle$ is the mth pure-vibrational eigenket and f is an appropriate function of the instantaneous moments of inertia given in terms of the normal-mode coordinates. Integration is effected by the generalized Gauss quadrature previously described.[7] The matrices $\vec{A}$, $\vec{B}$, $\vec{C}$, and $\vec{D}$ are symmetric, and $\vec{F}$ is skew symmetric. The straightforward construction of the matrix of Eq. (1) in the symmetric-top basis will be described in a full account to be published elsewhere.

As a minimal vibrational basis, we take the four lowest-energy states (0,0,0), (0,1,0), (0,0,1), and (1,0,0), where (v_1, v_2, v_3) gives the nominal[10] numbers of quanta in the Q_1, Q_2, and Q_3 vibrations, respectively. Numbering these states 1–4, we give the values of the vibrational matrix components of the rotational coefficients in Table I. The D_{nm} term and a term in the difference $A_{nm}-B_{nm}$ couple adjacent odd or adjacent even values of the molecular z-axis angular-momentum component quantum number K. The term in F_{nm} is the Coriolis coupling that splits levels with nonzero K in the presence of vibrational angular momentum.

We report our results in Tables II and III in the form of electric dipole-allowed transition frequencies (cm^{-1}) for the first dozen or so lines in the P, Q, and R branches of the ν_E fundamental.[11] A discussion of the term patterns and eigenfunctions will be given in the full report, but we mention here that for H_3^+ (but not D_3^+), the A_1 breathing mode is rotationally coupled to the E infrared-active mode for $J \geq 6$. This may have implications for the relaxation of the metastable (1,0,0) vibration state to (0,1,0), (0,0,1), and (0,0,0) at relatively low rotational excitation. Furthermore, a slight calculated splitting of some of the E levels at high J and low K in H_3^+ appears to indicate that a larger vibrational basis is required for accurate results when $J \gtrsim 5$ or 6. Calculations with a 10-member basis are in progress.

Since the D_3^+ amplitudes are smaller, the vibration-rotation interaction is less, and we expect our results to be more accurate than for H_3^+. We

TABLE II. Results of *ab initio* calculation of the H_3^+ rotation-vibration spectrum.[a]

P-Branch		^{p}Q-Branch		^{r}Q-Branch		R-Branch	
$^{p}P_1(1)E$	2452.277	$^{p}Q_1(1)E$	2539.963	$^{r}Q_1(6)E$	2526.808	$^{r}R_1(1)E$	2687.855
$^{p}P_2(2)E$	2374.398	$^{p}Q_1(2)E$	2548.592	$^{r}Q_0(1)A_2$	2525.417	$^{r}R_0(1)A_2$	2720.257
$^{p}P_1(2)E$	2367.786	$^{p}Q_2(2)E$	2550.053	$^{r}Q_2(6)E$	2518.993	$^{p}R_1(1)E$	2720.770
$^{p}P_3(3)A_2$	2295.215	$^{p}Q_3(3)A_2$	2561.062	$^{r}Q_1(2)E$	2515.678	$^{r}R_2(2)E$	2761.340
$^{p}P_2(3)E$	2292.806	$^{p}Q_2(3)E$	2563.684	$^{r}Q_0(5)A_2$	2512.940	$^{r}R_1(2)E$	2766.382
$^{p}P_1(3)E$	2292.550	$^{p}Q_4(4)E$	2568.927	$^{r}Q_0(3)A_2$	2512.467	$^{p}R_2(2)E$	2820.931
$^{r}P_0(3)A_2$	2292.696	$^{p}Q_1(3)E$	2568.698	$^{r}Q_1(3)E$	2510.340	$^{p}R_1(2)E$	2824.740
$^{r}P_1(3)E$	2259.636	$^{p}Q_5(5)E$	2578.497	$^{r}Q_1(5)E$	2510.276	$^{r}R_3(3)A_2$	2833.144
$^{p}P_1(4)E$	2231.452	$^{p}Q_3(4)A_2$	2576.178	$^{r}Q_1(4)E$	2506.769	$^{r}R_2(3)E$	2840.291
$^{p}P_2(4)E$	2224.872	$^{p}Q_6(6)A_2$	2588.877	$^{r}Q_2(3)E$	2504.093	$^{r}R_1(3)E$	2844.015
$^{p}P_3(4)A_2$	2219.512	$^{p}Q_2(4)E$	2592.898	$^{r}Q_2(5)E$	2504.002	$^{r}R_4(4)E$	2904.899
$^{p}P_4(4)E$	2215.838	$^{p}Q_4(5)E$	2597.411	$^{r}Q_2(4)E$	2501.479	$^{r}R_3(4)A_2$	2915.697

[a] Superscripts p, r denote $\Delta K = -1, +1$, respectively (in absorption) and P, Q, R denote $\Delta J = -1, 0, +1$ respectively; the numerical subscript is the initial (lower level) K value, and the number in parentheses is the initial J value. The letter beside the line symbol is the symmetry (in D_{3h}) of the rotation-vibration species. Line positions are in cm^{-1}.

TABLE III. Results of *ab initio* calculation of the D_3^+ rotation-vibration spectrum.[a]

P-Branch		${}^pQ$-Branch		${}^rQ$-Branch		R-Branch	
${}^pP_1(1)E$	1794.295	${}^pQ_1(1)E$	1837.941	${}^rQ_0(1)A_2$	1832.808	${}^rR_0(0)A_1$	1879.503
${}^pP_2(2)E$	1753.937	${}^pQ_1(2)E$	1840.648	${}^rQ_0(2)A_1$	1830.324	${}^rR_1(1)E$	1915.621
${}^pP_1(2)E$	1751.499	${}^pQ_2(2)E$	1841.308	${}^rQ_1(2)E$	1829.179	${}^rR_0(1)A_2$	1926.891
${}^rP_0(2)A_1$	1749.826	${}^pQ_3(3)A_1$	1843.996	${}^rQ_0(3)A_2$	1827.295	${}^pR_1(1)E$	1927.091
${}^pP_3(3)A_1$	1713.196	${}^pQ_3(3)A_2$	1844.682	${}^rQ_1(3)E$	1826.694	${}^rR_2(2)E$	1954.145
${}^pP_3(3)A_2$	1713.062	${}^pQ_2(3)E$	1845.481	${}^rQ_0(6)A_1$	1824.874	${}^rR_1(2)E$	1955.809
${}^pP_2(3)E$	1711.907	${}^pQ_4(4)E$	1847.098	${}^rQ_2(3)E$	1824.743	${}^pR_2(2)E$	1974.883
${}^pP_1(3)E$	1711.533	${}^pQ_1(3)E$	1847.008	${}^rQ_0(4)A_1$	1824.569	${}^pR_1(2)E$	1976.123
${}^rP_0(3)A_2$	1711.492	${}^pQ_3(4)A_2$	1849.469	${}^rQ_1(6)E$	1824.128	${}^rR_0(2)A_1$	1976.690
${}^rP_1(3)E$	1700.063	${}^pQ_5(5)E$	1849.709	${}^rQ_1(4)E$	1824.078	${}^rR_3(3)A_2$	1992.047
${}^rP_0(4)A_1$	1676.664	${}^pQ_3(4)A_1$	1851.342	${}^rQ_0(5)A_2$	1823.285	${}^rR_3(3)A_1$	1992.249
${}^pP_1(4)E$	1675.878	${}^pQ_6(6)A_2$	1852.293	${}^rQ_1(5)E$	1822.716	${}^rR_2(3)E$	1994.184

[a] See footnote to Table II.

therefore concentrate on D_3^+ in our comparison with observations. The principal errors in the calculation are in the rotationless vibrational transition frequency ν_0 (calculated to be 2515.990 cm^{-1} for H_3^+, 1826.391 cm^{-1} for D_3^+) and the equilibrium internuclear distance R_e (calculated to be $1.657\,37a_0$). The error in ν_0 is additive and the error in R_e enters as a factor of the rotational constants (roughly proportional to R_e^{-2}). Thus we may adjust the *ab initio* line positions ν by writing

$$\nu_{\mathrm{adj}} = r\nu + q,$$

where $r = (R_{\mathrm{calc}}/R_e)^2$ and $q = (1-r)\nu_0 + \Delta\nu$. In Table IV we give adjusted values of the first four D_3^+ line positions in the P branch. An excellent fit to observations[12] is obtained for $\Delta\nu = 8.937\ \mathrm{cm}^{-1}$ and $r = 1.016\,394$ [corresponding to an estimated R_e of $1.644a_0$ (compare $1.650a_0$ obtained in Ref. 5 and in an "improved" ACI calculation reported in Refs. 4 and 6)]. The agreement of observed and adjusted line positions is remarkable in view of the fact that the ${}^rP_0(2)\ A_1$ line at 1757.478 cm^{-1} has an upper state that is shifted ~ 1.4 cm^{-1} by l-type doubling. In the case of H_3^+, the observed lines[13] are generally at positions 5 and 6 cm^{-1} higher than the *ab initio* values. We conclude that our method for the rotation-vibration calculation is satisfactory and that future work should concentrate on refinement of methods for obtaining accurate and consistant potential-energy surfaces. Analysis of both the H_3^+ and D_3^+ theoretical and observed spectra for an accurate R_e value that will allow determination of the H_2D^+ pure-rotation spectrum is in progress.

TABLE IV. Adjustment for errors in the pure vibrational transition frequency and equilibrium internuclear distance for D_3^+.

Transition	*Ab Initio*	Adjusted[a]	Observed[b]
${}^pP_1(1)\ E$	1794.295	1802.706	1802.716
${}^pP_2(2)\ E$	1753.937	1761.686	1761.709
${}^pP_1(2)\ E$	1751.499	1759.208	1759.205
${}^rP_0(2)\ A_1$	1749.826	1757.508	1757.478

[a] See Eq. (2). [b] Reference 12.

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