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Rotational spectrum and structure of Ne–C$_6$H$_6$–H$_2$O, an aromatic sandwich

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Low $J(J=1\rightarrow5)$ rotational spectra of seven isotopomers of Ne–C$_6$H$_6$–H$_2$O trimer have been observed with a Balle/Flygare Fourier transform microwave spectrometer. The trimer is found to be a symmetric top with a B_0, D_J, and D_{JK} in the parent of 959.3504(1) MHz, 2.425(2) kHz, and 13.385(5) kHz. The benzene is sandwiched between Ne and H$_2$O, both of which lie on the C$_6$ axis of benzene. Substitution analysis gives the neon and oxygen distances from the trimer center of mass (c.m.) to be 3.324 and 3.454 Å, respectively. The Ne to c.m. (C$_6$H$_6$) and c.m. (C$_6$H$_6$) to c.m. (H$_2$O) distances thereby determined are 3.391 and 3.334 Å, respectively. Those in the corresponding dimers are 3.458 and 3.329 Å, giving a decrease in the trimer of 0.067 Å in the Ne to c.m. (C$_6$H$_6$) distance and an increase of 0.005 Å in c.m. (C$_6$H$_6$) to c.m. (H$_2$O). Otherwise the state of the water in the dimer does not appear to be materially affected by addition of the Ne.

In recent years rotational spectra have been studied for several dimers in which the π electrons of benzene interact with a rare gas (Rg) atom[1,2] or a small molecule.[3–7] Also, rotationally resolved electronic spectra have been observed for dimers and trimers incorporating C$_6$H$_6$ (Refs. 8–10) or C$_5$H$_5$ (Ref. 11) with one or two He or Ne atoms. Several *ab initio* studies of the Rg–C$_6$H$_6$ interactions have appeared as well.[12–14] However, rotational spectra have not been reported for trimers where the π electrons interact with species on both faces of the ring. Here we describe observations of such a case, the Ne–C$_6$H$_6$–H$_2$O trimer, with benzene sandwiched between a Ne atom and an H$_2$O molecule. The trimer may be viewed as a composite of the Ne–C$_6$H$_6$ and C$_6$H$_6$–H$_2$O dimers. As such it is of interest to compare the trimer with the two dimers. Our results show that "weak dimer" formation at one face has a relatively small effect upon the interactions in the "strong dimer" at the other face and vice versa.

The rotational spectrum of Ne–C$_6$H$_6$–H$_2$O trimer was observed with a Balle/Flygare Fourier transform microwave spectrometer.[15] Initial observation of the trimer was serendipitous in that the $m=0$, $J=1\rightarrow2$ lines of Ne–C$_6$H$_6$–HDO were found during a search for the $m=1$, $J=0\rightarrow1$ transition of the C$_6$H$_6$–D$_2$O dimer.[4] Unlike the dimer lines, they could not be seen when using pure He or Ar as the carrier gas. The trimer lines were observed with 1 to 2 atm backing pressure of first run neon (70% Ne and 30% He) as carrier. The other ingredients were added by bubbling roughly 1% and 2% of the carrier gas through C$_6$H$_6$ and H$_2$O at ambient conditions. All the lines were tested for their dependence on the presence of Ne, C$_6$H$_6$ and H$_2$O. Once the correct assignments were made for the Ne–C$_6$H$_6$–HDO species and fitted, low J spectra were predicted and observed for the other six isotopomers.

The dynamic state of the H$_2$O in the trimer and the overall nature of the rotational spectrum for the trimer appear to be basically the same as in the C$_6$H$_6$–H$_2$O dimer which has been studied in some detail.[4,5] Even though H$_2$O and its isotopic species are asymmetric tops, their nearly free internal rotation in the dimer leads to internal rotor

states with symmetric top type spectra, of which the ground $m=0$ and first excited $m=1$ states have been reported.[4] The spectra summarized in Table I correspond to $m=0$ progressions. Measurements of $m=1$ progressions are in progress for several species.

The $m=0$ transitions of each isotopomer were fitted by the standard symmetric top equation

$$v=2\bar{B}(J+1)-4D_J(J+1)^3-2D_{JK}(J+1)K^2. \quad (1)$$

The fitting included rotational transitions from $J=1\rightarrow2$ through $J=5\rightarrow6$ for ^{20}Ne–C$_6$H$_6$–H$_2$O/D$_2$O/HDO/H$_2$^{18}O and through $J=4\rightarrow5$ for ^{22}Ne–C$_6$H$_6$–H$_2$O/D$_2$O/HDO. In the fitting 18 transitions were included for each of the first group of isotopomers and 13 for the second. The standard deviation for each of the fits was within 2 kHz. The rotational and centrifugal distortion constants determined by the fits are listed in Table I.

The overall effective geometry of the trimer is readily apparent from the symmetric top spectra of its isotopomers, and their rotational constants. They require that the sixfold axis of the benzene be the a axis of the trimer and that the Ne and H$_2$O be on that axis.[4] Substitution analysis with ^{20}Ne–C$_6$H$_6$–H$_2$O as the parent,[16] gives $|a_{Ne}|$ to be 3.324 Å and $|a_O|$ to be 3.454 Å, placing the Ne and H$_2$O at opposite faces of the benzene as shown in Fig. 1. The orientation of the H$_2$O in the trimer is essentially the same as that in the dimer.[4] The oxygen is away from the benzene ring, as shown by the systematic decrease in $\bar{B}$ (Table I) upon substituting HDO, D$_2$O, and H$_2$^{18}O. Also, substitution analysis of $\bar{B}$ for the H$_2$O, D$_2$O, and H$_2$^{18}O isotopomers shows that the C$_2$ axis of the water is at an average angle of 35° with the a axis compared to 37° in the dimer.

The c.m. (H$_2$O) position in the trimer is needed for comparative purposes. It was obtained from the oxygen substitution position by projection of the O to c.m. (H$_2$O) distance (0.0666 Å) onto the a axis, as was done for the dimer.[4] This gives a_{H_2O} to be 3.401 Å. Moreover, by using a pseudo triatomic approach and the first moment condition, one can write

TABLE I. Symmetric top rotational constants determined from the transitions observed for the Ne–C_6H_6–H_2O isotopomers.[a]

Isotopomer	B (MHz)	D_J (kHz)	D_{JK} (kHz)	σ[b] (kHz)
Ne–C_6H_6–H_2O	959.3504(1)	2.425(2)	13.385(5)	1.4
Ne–C_6H_6–HDO	944.4244(1)	2.332(1)	14.925(5)	0.9
Ne–C_6H_6–D_2O	927.2092(2)	2.237(3)	13.21(2)	1.8
Ne–C_6H_6–$H_2{}^{18}O$	918.3755(1)	2.146(2)	12.04(1)	1.1
^{22}Ne–C_6H_6–H_2O	921.3840(1)	2.349(1)	12.744(7)	0.8
^{22}Ne–C_6H_6–HDO	907.0947(7)	2.24(3)	13.57(7)	3.2
^{22}Ne–C_6H_6–D_2O	890.6366(3)	2.12(1)	12.62(3)	1.3

[a]The numbers in parentheses are the standard deviation of the constant.
[b]Standard deviation of the fit to frequencies observed for the isotopomer.

$$a_{Ne}M_{Ne}+a_{Bz}M_{Bz}+a_{H_2O}M_{H_2O}=0, \qquad (2)$$

where M_X is the mass of X and a_X is the distance, with appropriate sign, of c.m. (X) along the a axis from the c.m. of the trimer. Thereby we find 0.067 Å for a_{Bz} and determine the c.m. separations in the trimer to be 3.391 Å for Ne–C_6H_6 and 3.334 Å for C_6H_6–H_2O. These values we now compare to the corresponding distances in the dimers.

For C_6H_6–H_2O the low-J rotational spectrum and substitution analysis[4] gave a c.m. (C_6H_6) to c.m. (H_2O) distance of 3.329 Å. This is 0.005 Å shorter than in the trimer, which is surprising inasmuch as the reverse has been found in several linear trimers containing the HCN dimer.[17] However, the apparent effect is small for C_6H_6–H_2O and probably within model error.

In the case of Ne–C_6H_6, the rotational spectrum has not been reported. Bauder and co-workers[13] searched unsuccessfully for it and suggested that either the dipole moment or the binding energy is very low. However, sub-Doppler UV spectroscopy has given 3.460 Å for the Ne to c.m. (C_6H_6) distance in the dimer.[9] In addition, our observation of the trimer containing Ne–C_6H_6 led us to think it should be possible to observe the rotational spectrum of the dimer. In fact we have now done this[18] using a 5 to 6 μs

microwave pulse, indicating a low dipole moment. The experimental symmetric top $\bar{B}$ of 1810.2550(6) MHz gives a Ne to c.m. (C_6H_6) distance of 3.458 Å, in close agreement with the UV work. With these determinations, one sees that the Ne–C_6H_6 distance has contracted by 0.067 Å in the trimer. Evidently the weak Ne–C_6H_6 interaction (100 cm^{-1})[12] has much less influence on the strong C_6H_6–H_2O interaction (1300 cm^{-1})[19] than vice versa.

Other evidence strongly supports the view that the C_6H_6–H_2O dimer is little affected by addition of the Ne to the other face of the benzene. In the $m=1$, K progressions of the dimer, the $K=+J$ components are substantially and systematically displaced to frequencies above the $m=0$, K progressions by an as yet undetermined perturbation.[4] The trimers display the same effect. For C_6H_6–HDO the deuterium quadrupole interaction gives a triplet hyperfine structure (hfs) in the $J=0\rightarrow1$ transition with $\chi_{aa}(D) =168.3$ kHz showing that the O–D axis is at an angle of $33.9°$ to the a axis, which means that the deuterium is preferentially hydrogen bonded to the benzene. Similar hfs in the $J=0\rightarrow1$ transition of the parent trimer at 1888.840 MHz (Ref. 20) with $\chi_{aa}(D)=165.5$ kHz gives an angle of $34.2°$.

Further work on the Rg–C_6H_6–H_2O trimers is in progress. Symmetric top $m=0$ progressions have been observed for several isotopomers with Ar and Kr as the rare gas. Also, the $m=1$ transitions have been observed for some isotopic species of the trimers with Ne, Ar, and Kr. A full account of our results is planned for these three systems as well as for the Ne–C_6H_6 dimer.[18]
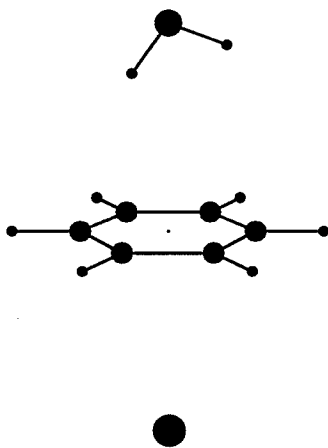
ACKNOWLEDGMENTS

FIG. 1. Molecular geometry of the $m=0$ state of the Ne–C_6H_6–H_2O trimer. The nearly free internal rotational of the water molecule makes the trimer behave like a symmetric top. The Ne to c.m. (C_6H_6) and c.m. (C_6H_6) to c.m. (H_2O) distances are found to be 3.391 and 3.334 Å, respectively.

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[20] Attainment of this low frequency required modification of the Fabry–Perot, cavity, the details of which will be reported later.