tion of the HDA and LDA $S(Q)$ functions. Several combinations of the $S(Q)$ of the HDA and LDA structures are plotted in Fig. 1, B (neutron data) and D (x-ray data); also plotted are the data from the sample annealed at 105 K. The annealed structures factors cannot be produced by any combination of LDA and HDA. We note the region in Fig. 1D where the x-ray curves intersect at 2.05 Å$^{-1}$, the peak is at 2.09 Å$^{-1}$ for the annealed sample, and there is only a small error in the data in this region.

The measured total structure factors of the quenched states were transformed into real-space radial distribution functions, and the several representative data sets are plotted in Fig. 4A for the neutron experiments and in Fig. 4B for the x-ray experiments. Although the neutron data are predominantly weighted toward the hydrogen-hydrogen and oxygen-hydrogen correlations and the x-ray data are predominantly weighted toward the oxygen-oxygen correlations, the major real-space structural trends upon annealing can be seen in both sets of data, and they are generally described by short- to intermediate-range structural changes between 4 and 8 Å. The described by short- to intermediate-range in both sets of data, and they are generally structural trends upon annealing can be seen predominantly weighted toward the oxygen–hydrogen correlations and the x-ray data are substantially increase in the intensity of the broad peak centered at $\sim 6.4 \text{ Å}$ shifts systematically to greater distance with increasing anneal temperature. In addition, a substantial increase in the intensity of the broad peak centered at $\sim 4.5 \text{ Å}$ with increasing anneal temperature is noted. The hydrogen-bonded oxygen–oxygen distance, given by the position of the first peak in the x-ray $G(r)$, shortens systematically through the transformation between each amorphous form and ranges from 2.80 Å in the unannealed HDA phase to 2.76 Å in the final lowest density phase; this is consistent with measured Ramana data (23).

We annealed HDA ice at several temperatures below 113.4 K (i.e., the recorded transition temperature to the LDA form). It is seen from the position of the FSDP in the static structure factor that the transition from the HDA form to the LDA form can proceed in a structurally continuous manner through a series of intermediate, apparently metastable amorphous forms. Several of these metastable forms were observed, and detailed radial distribution functions were compared at temperature $T = 40 \text{ K}$. It is reasonable to expect that, in principle, a continuous distribution of recoverable forms between HDA and LDA ice is possible. At any $T < 113.4 \text{ K}$, the thermal energy is insufficient to overcome the potential barriers that define a particular metastable structure. This is what is in general expected for the existence of any metastable phase and indicates that the transformation between the poly-amorphs of ice may be somewhat complex. From the radial distributions functions presented here, it appears that the transition predominantly evolves on the short to intermediate length scale; that is, major structural changes occur between 4 and 8 Å, and more subtle changes also occur on the hydrogen bond length scale. These data may have important implications regarding the current understanding of the structural relation between a low-density liquid water and LDA ice, and a high-density liquid water and HDA ice (2, 23–25). These results may also impact on the character of the transformation from ice lh to HDA (5, 26), the HDA-LDA mixture model (5), and the relations between normal water and HDA. In addition, understanding structural variations in amorphous water, particularly the predominant length scales over which such variations occur, may provide a basis for understanding biomolecular hydration and cryopreservation.

**References and Notes**


**The Vibration-Rotation Emission Spectrum of Free BeH$_2$**

Peter F. Bernath,*1 Alireza Shayesteh,*1 Keith Tereszczuk,1 Reginald Colin2

The gaseous BeH$_2$ molecule has been synthesized by means of an electrical discharge inside a high-temperature furnace and identified with infrared emission spectroscopy. The antisymmetric stretching mode $v_3$ has been detected near 2179 reciprocal centimeters. The BeH$_2$ molecule has a linear, symmetric structure with an $r_0$ BeH bond length of 1.333761(2) angstroms. Heating BeH$_2$ solid results in decomposition to the elements, not the production of BeH$_2$ vapor.

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With only six electrons, BeH$_2$ is a favorite target molecule for testing new ab initio quantum chemical methods [for example, (1–4)]. Despite this strong interest in BeH$_2$, the free molecule remains unknown. It has been detected previously through its infrared spectrum near 2179 reciprocal centimeters.

The BeH$_2$ molecule has a linear, symmetric structure with an $r_0$ BeH bond length of 1.333761(2) angstroms. Heating BeH$_2$ solid results in decomposition to the elements, not the production of BeH$_2$ vapor.

The insertion of ground-state Be atoms into the target molecule for testing new ab initio quantum chemical methods [for example, (1–4)]. Despite this strong interest in BeH$_2$, the free molecule remains unknown. It has been detected previously through its infrared spectrum.
an alumina tube 5 cm (outside diameter) by 120 cm long was heated to 1500°C by a CM Rapid Temp furnace. The water-cooled ends of the tube were sealed with CaF2 windows. A slow flow of helium (about 20 torr) and hydrogen (about 10 torr) was passed through the cell. A dc discharge (2.5 kV, 333 mA) was struck between stainless-steel tube electrodes inside the alumina tube but outside the hot zone. Powdered Be metal (5 g) was placed inside a small zirconia boat in the center of the hot zone. The emission from the furnace was focused with a CaF2 lens into the entrance aperture of a Bruker IFS 120 HR Fourier transform spectrometer. One hundred scans were recorded at a resolution of 0.03 cm⁻¹ with a liquid N₂-cooled InSb detector. The spectral region was limited to 1800 to 2900 cm⁻¹ by the detector response and a long-wave-pass filter.

The IR emission spectra contain numerous atomic and molecular emission lines, as well as atmospheric absorption features from CO₂ and H₂O (Fig. 1). The strongest emission lines are due to the BeH₂ free radical (14), for which the R-head of the v3 fundamental band can be seen (asterisks) at the left side of the figure. In addition, a series of lines spaced by about 8 cm⁻¹ in intensity and 8 cm⁻¹ in wavelength were assigned to the R branch of the antisymmetric stretching mode v4, as well as many unassigned emission lines presumably from BeH₂ hot bands, which can be seen.

Fig. 1. A portion of the infrared emission spectrum of BeH₂. The R-branch of the antisymmetric stretching mode v4 is indicated. The lines of the v = 1 → 0 fundamental band of BeH₂ are marked with asterisks. The absorption of atmospheric CO₂, as well as many unassigned emission lines, are distinguished in the figure [see Table S1 for a complete list of line assignments (15)]. The lines listed in Table S1 have an accuracy of better than 0.001 cm⁻¹ based on a calibration with the BeH₂ lines, which were calibrated with CO in a previous spectrum (14). A fit of these lines to the customary rotational energy level expression (16), E = v + B(J + 1) - D(J(J + 1)² + H[J(J + 1)]), results in the spectroscopic constants shown in Table 1.

The lines are assigned to the v4 (σg) antisymmetric stretching mode of the linear BeH₂ molecule for several reasons:

1) The 3:1 intensity ratio of adjacent lines is due to the ortho-para nuclear spin statistical weights associated with the nuclear spin I = 1/2 H nuclei (17). This intensity alternation is consistent with a linear, symmetric structure (D₂h symmetry).

2) The gas-phase band origin of 2178.859 cm⁻¹ matches the Ar matrix value of 2159 cm⁻¹ (5), if a matrix shift is taken into account.

3) Martin and Lee’s (11) high-level ab initio calculation of the quartic force field predicts a band origin of 2167 cm⁻¹ for v3, as well as B₀' = 4.660 cm⁻¹ for the lower state, B₀' = 4.590 cm⁻¹ for the upper state, and D₂ of 1.0 × 10⁻⁴ cm⁻¹, all in good agreement with the values presented in Table 1. The predicted α₀ value of 0.070 cm⁻¹, in particular, agrees very well with the observed B₀' - B₀' value of 0.069 cm⁻¹.

The B₀' value shown in Table 1 implies an r₀ bond length of 1.333761(2) Å, close to the rₑ equilibrium bond length value of 1.3417 Å for BeH₂ (12). The unpaired electron in the BeH₂ free radical is in a nonbonding sp hybrid orbital, so the formation of a second bond with an H atom changes the bond length only slightly. The best ab initio value for rₑ is 1.3397 Å (11), and the corresponding r₀ value is 1.3324 Å (11).

Information about the other vibrational modes of BeH₂ can be deduced from the line positions of the v1 mode. There is a small perturbation in the J' = 22 energy level [the observed minus calculated values are 0.025 cm⁻¹ for the R(21) and P(23) lines as compared with the typical values of <0.001 cm⁻¹ (15)] that is likely due to an interaction with the 3v₁ (σg) vibrational level. This perturbation also confirms our rotational numbering for the v₁ band. Our spectra still contain a number of unassigned lines (Fig. 1), many of which we expect are BeH₂ hot bands. A complete assignment currently in progress should ultimately allow an equilibrium molecular structure to be derived.

References and Notes
15. Supplementary material is available on Science Online.
18. We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for support.

Supporting Online Material
www.sciencemag.org/cgi/content/full/297/5585/1323/DC1
Table S1

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Table 1. Spectroscopic constants for the v₁ vibrational mode of BeH₂ (in cm⁻¹). One standard deviation in the last digits quoted is in parentheses. Single primes refer to the upper state and double primes to the lower state.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁</td>
<td>2178.8560(24)</td>
</tr>
<tr>
<td>B'</td>
<td>4.632178(13)</td>
</tr>
<tr>
<td>D'</td>
<td>1.03286(36) × 10⁻⁴</td>
</tr>
<tr>
<td>H'</td>
<td>2.6152(11) × 10⁻⁸</td>
</tr>
<tr>
<td>B''</td>
<td>4.701380(13)</td>
</tr>
<tr>
<td>D''</td>
<td>1.04942(34) × 10⁻⁴</td>
</tr>
<tr>
<td>H''</td>
<td>2.67720(10) × 10⁻⁸</td>
</tr>
</tbody>
</table>