Noble Gas Complexes with BeO: Infrared Spectra of NG–BeO (NG = Ar, Kr, Xe)

Craig A. Thompson and Lester Andrews*

Department of Chemistry, McCormick Road
University of Virginia
Charlottesville, Virginia 22901

Pulsed-laser-ablated beryllium atom reactions with small molecules such as H_2, O_2, CO, and N_2 have recently produced new species for study with matrix infrared spectroscopy.[1-4] Reactions involving beryllium and oxygen are of particular interest because of theoretical predictions that the highly ionic BeO product molecule will form interesting complexes such as Ar–BeO, OC–BeO, and N_2–BeO.[5,6] The molecule BeO is also of considerable importance,[7-9] but matrix studies of BeO will be complicated by the formation of the noble gas compounds. Laser-ablated beryllium atoms were condensed with molecular oxygen and the noble gases argon, krypton, and xenon. As predicted, the noble gas compounds NG–BeO (NG = Ar, Kr, Xe) have been observed. The other beryllium–oxygen product species Be_2O_2 (ring), BeO_2, Be_2O_2 (linear), and BeO_3 will be discussed in a forthcoming paper.[2]

The apparatus for pulsed-laser-ablation matrix-isolation spectroscopy has been described earlier.[10,11] Mixtures of $Ar:O_2$ (100:1 to 400:1) were codeposited at 10 ± 1 K with laser-ablated beryllium atoms using a Nd:YAG laser focused on a rotating 1-cm × 1-cm beryllium target (Johnson-Matthey). Laser powers of about 50 mJ/pulse at the target appeared to give optimum results. For the formation of Kr–BeO and Xe–BeO, oxygen (0.5–3.0%) and a noble gas (1.0–10.0%) were added to argon and codeposited with beryllium atoms. Samples were subjected to UV photolysis and annealing, and more spectra were recorded at 0.5-cm^{-1} resolution and ± 0.1-cm^{-1} accuracy on a Nicolet 750 FTIR instrument.

Figure 1 gives the spectra for the BeO stretching region from 1530 to 1380 cm^{-1}. This region contains the new product bands discussed here as well as the BeO_2 antisymmetric stretching absorption which will be used for comparison. The spectra in Figure 1a–c are from beryllium reactions with molecular oxygen in an argon matrix. The peak marked 1 in Figure 1a occurs at 1526.1 cm^{-1}; its ^{18}O counterpart marked 2 appears in Figure 1b at 1497.7 cm^{-1}. The new band belongs to a species which contains one oxygen atom because the $^{16,18}O_2$ experiment shown in Figure 1c produced the same bands without intermediate, mixed-isotopic components. In contrast, the BeO_2 peak in Figure 1a shows that a molecule with more than one oxygen atom gives a multiplet upon reaction with $^{16,18}O_2$ samples.

The bands 1 and 2 are not due to diatomic BeO for two reasons. (1) the 1526.1-cm^{-1} band is blue-shifted from the gas-phase BeO fundamental at 1463.7 cm^{-1}.[12] This blue shift would be abnormal for an ionic molecule such as BeO with a large dipole moment. Ionic molecules usually experience a significant red argon matrix
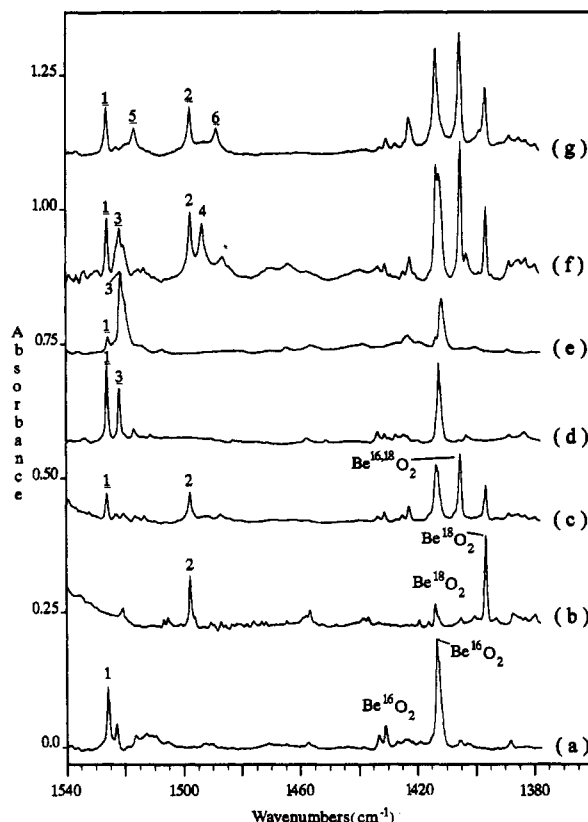
(1) Tague, T. J., Jr.; Andrews, L. *J. Am. Chem., Soc.*, to be published.
(2) Thompson, C. A.; Andrews, L., to be published.
(3) Tague, T. J., Jr.; Andrews, L.; Davy, R. D., to be published.
(4) Thompson, C. A.; Andrews, L., to be published.
(5) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988,** *110*, 8007.
(6) Frenking, G.; Koch, W.; Collins, J. R. *J. Chem. Soc., Chem. Commun.* **1988,** 1147.
(7) Schaefer, H. F., III. *J. Chem. Phys.* **1971,** *55*, 176.
(8) Langhoff, S.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1986,** *84*, 4474.
(9) Watts, J. D.; Urban, M.; Bartlett, R. J., to be published.
(10) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991,** *95*, 8697.
(11) Hassanzadeh, P.; Andrews, L. *J. Phys. Chem.* **1992,** *96*, 9177.
(12) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

Figure 1. Infrared spectra of NG + Be + O_2 reaction products (NG = Ar, Kr, Xe) in solid argon at 10 ± 1 K. (a) Be + $^{16}O_2$ + Ar (matrix gas); (b) Be + $^{18}O_2$ + Ar (matrix gas); (c) Be + $^{16}O_2$,$^{16,18}O_2$,$^{18}O_2$ (1:2:1) + Ar (matrix gas); (d) Be^{16}O + Kr (1% in argon); (e) Be^{16}O + Kr (10% in argon); (f) Be + $^{16,18}O_2$ + Kr (2.5% in argon); and (g) Be + $^{16}O_2$ + Xe (1% in argon).

shift; however, the spectrum is free of product absorptions other than BeO_2 down to 1310 cm^{-1}. (2) The observed $^{16}O/^{18}O$ ratio (1.018 96) is slightly lower than the calculated diatomic harmonic ratio (1.020 69) and the diatomic ratio corrected for anharmonicity (1.020 34). This ratio indicates mechanical coupling of Be with another atom in an "antisymmetric" Ar–Be–O vibrational mode. The major Ar interaction is with Be and not the BeO molecule as a whole. A uniform argon interaction with the entire BeO molecule would indeed give the diatomic $^{16}O/^{18}O$ ratio.

The failure to observe isolated BeO, along with theoretical predictions of stable noble gas compounds absorbing in this region, leads to the conclusion that 1 and 2 belong to Ar–BeO. In fact, the bands show excellent agreement with ab initio calculations that predict a strong infrared absorption for Ar–BeO blue-shifted substantially from the BeO diatomic fundamental.[5] Observed frequencies for the NG–BeO species are collected in Table 1, along with theoretical harmonic frequencies.

In another set of experiments, ceramic beryllia (General Ceramics, Inc.) was ablated and condensed with matrix gas under similar conditions. This experiment produced relative yields of all products similar to the Be + O_2 reactions. An experiment using the BeO ceramic and 1% $^{18}O_2$ in argon gave stronger Be$^{18}O_2$ and Ar–Be^{18}O absorptions than the Be$^{16}O_2$ and Ar–Be^{16}O bands. It appears that essentially complete atomization of the BeO ceramic material is occurring.

Krypton and xenon experiments are of interest because they help to explain the nature of noble gas interactions with BeO, which have been described as relatively strong charge-induced dipole interactions.[5,6] The spectra for three reactions with krypton and one reaction with xenon diluted in argon are given in Figure 1d–g. Figure 1d shows the new krypton absorption band at 1521.8 cm^{-1} corresponding to Kr–Be^{16}O marked 3. The counterpart for

Table 1. Observed and Calculated Antisymmetric NG–Be O Stretching Frequencies (cm^{-1}) for Ar–BeO, Kr–BeO and Xe–BeO

	(^{16}O)	(^{18}O)	^{16}O/^{18}O ratio
Ar–BeO			
observed	1526.1	1497.7	1.018 96
calculated[a]	1516.0	1488.4	1.018 54
Kr–BeO			
observed	1521.8	1493.5	1.018 95
calculated[a]	1510.1	1482.6	1.018 55
Xe–BeO			
observed	1516.7	1488.6	1.018 88
calculated[a]	1500.9	1473.4	1.018 66

[a] Using MP2 theory, ref 13.

the Kr–Be^{18}O species produced in the Be + ^{16,18}O$_2$ + Kr experiment appeared at 1493.5 cm^{-1} and is marked 4 in Figure 1f. A decrease in the absolute yield of Ar–BeO in experiments that contain krypton or xenon is expected. Figure 1d shows that with 1% krypton a ratio of argon species 1 to krypton species 3 of 3:2 is observed. Notice in Figure 1e that with 10% krypton the absolute yield of 1 has dramatically decreased and the absolute yield of the 3 band has increased, giving relative band intensities of 1:7. The contrasting behavior of the BeO$_2$ band is also of interest. In experiments with argon and oxygen, BeO$_2$ appeared at 1413.2 cm^{-1}; the band shifted only slightly to 1411.5 cm^{-1} and broadened in the 10% krypton experiment. The change in the absolute and relative intensities of 1 and 3 and the failure to observe substantial krypton shifts for BeO$_2$ together indicate that 3 is complex Kr–BeO, where Kr is competing favorably with Ar for bond formation to BeO. In pure krypton, the Kr–Be^{16}O and Kr–Be^{18}O bands were shifted to 1511.8 and 1483.6 cm^{-1}, respectively.

The results of a 1% xenon experiment in Figure 1g are analogous to those of the krypton experiment, yielding a ^{16}O species at 1516.7 cm^{-1} marked 5 and an ^{18}O species at 1488.6 cm^{-1} marked 6. The intensity of the 5 band is greater than that of 1 in the 1% xenon experiment, indicating that Xe is winning the competition with Ar, even with Ar in considerable excess, for binding to BeO. The Xe–Be^{16}O and Xe–Be^{18}O bands were observed at 1498.3 and 1470.5 cm^{-1}, respectively, in pure xenon.

Photolysis of the samples with a medium-pressure mercury arc lamp caused no change in the NG–BeO species. Annealing samples which contained either 1 and 3 or 1 and 5 appeared to cause both bands to decrease in proportion. This seems to indicate that all of the noble gas complexes react with the same species, such as unreacted Be and O atoms, that are allowed to diffuse through the matrix.

The dissociation energies and infrared intensities calculated for Ar–BeO, Kr–BeO, and Xe–BeO are 7, 10, and 13 kcal/mol and 34, 36, and 31 km/mol, respectively.[13] These compounds are stable, and the increasing band absorbances with Kr and Xe show preferential formation of the more stable Kr and Xe complexes in an argon matrix. The calculations also predict the more strongly bound Xe–BeO complex to have the lowest BeO frequency or to be less blue-shifted from the BeO diatomic molecule than the less strongly bound Ar–BeO complex.[13] The experimental and theoretical periodic trends are in excellent agreement, as shown in Table 1.

In summary, we have characterized by matrix infrared spectroscopy three noble gas compounds of the form NG–BeO (NG = Ar, Kr, Xe), including their isotopic NG–Be^{18}O counterparts. The trend in observed NG–BeO antisymmetric stretching frequencies is consistent with MP2/ECP calculations on these heavy-atom systems.[13] The ^{16}O/^{18}O ratios define an antisymmetric vibration of Be between oxygen and a heavy atom. The general positions of the observed bands, as well as those of the absolute and relative product band yields, are in excellent agreement with calculations that predict increasing interaction between the noble gas and BeO from Ar to Kr to Xe. All experimental evidence supports previous predictions that these molecules arise from strong induced dipole interactions. Furthermore, it appears that BeO, an extremely strong Lewis acid, forms the strongest neutral argon complex prepared to date.

(13) Veldkamp, A.; Frenking, G. *J. Am. Chem. Soc.*, submitted for publication.