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The Intramolecular Mode in Isotopically Substituted NO^+ β- and β''-Alumina

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Single crystals of ^{15}N-substituted NO^+ β- and β''-alumina were prepared and Raman scattering spectra of the nitrosonium intramolecular stretching mode were measured. The harmonic frequency and the cubic anharmonic force constant were calculated using these and similar data from the naturally abundant nitrosonium aluminas. Differences in the calculated values between the β and β'' system were attributed to structural differences in the conduction planes. © 1985 Academic Press, Inc.

Introduction

Symmetry-based vibrational mode assignments in nitrosonium (NO^+) β- and β''-alumina have been made of all observed modes resulting from nitrosonium ion motion (*1*). The fundamental vibrational transition frequencies of the nitrosonium ion in β- and β''-alumina allow a comparison of the properties of NO^+ in these two crystals and, indirectly, the potential energy environment of the NO^+ site in the conduction planes in β- and β''-alumina. These frequency values combined with the fundamental transition frequencies of the intramolecular mode of isotopically substituted nitrogen-15 nitrosonium ions can provide information concerning the shape of the vibrational potential energy function. This information is most easily obtained by calculating the harmonic frequency and the cubic anharmonic force constant from the measured fundamental transition frequencies and the calculated reduced masses of the nitrosonium ion and its isotopically labeled counterpart.

Experimental

Crystals of $^{15}NO^+$ β- and β''-alumina were prepared following the method of Radzilowski and Kummer (*2*) with some modifications as previously described (*1*). The only change in the experimental procedure was the use of $Na^{15}NO_3$ in the preparation of $^{15}NOCl$. Eight grams of 95% ^{15}N-labeled $NaNO_3$ were used to prepare the $^{15}NOCl$ from which $^{15}NO^+$ β-alumina samples were obtained, while the NOCl used in the production of the $^{15}NO^+$ β''-alumina samples was prepared from 2 g of 99% ^{15}N-labeled $NaNO_3$ and 6 g of unlabeled $NaNO_3$.

It is important to note that the crystal samples of β''-alumina from which the $^{15}NO^+$ β''-alumina was prepared were grown from different melts at the Oak Ridge National Laboratory. Magnesium was used to stabilize the β''-phase in both

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cases. The average sample size was 5.0 × 1.5 × 0.5 mm, since preliminary studies indicated that thin samples undergo much better ion exchange. The sample surfaces received only a minimum of polishing after removal from an NOCl · $AlCl_3$ melt due to their fragility. Samples were oriented with a polarizing microscope so that the *c* axis (optic axis) was perpendicular to the propagation directions of the incident and scattered radiation. No attempt was made to locate the crystallographic axes perpendicular to the *c* axis, and the symbols *a* and *a'* which are used in the figures to designate a Raman scattering geometry are arbitrary, mutually orthogonal axes which are themselves orthogonal to the *c* axis. Raman spectra were recorded with a Spex Ramalog 5 spectrometer using the 488.0-nm line of an argon-ion laser for excitation at 500 mW. The spectra were recorded with a spectral bandpass of 4 cm^{-1}.

Data

Figure 1 shows an *a*(*cc*)*a'* experiment comparing the frequency of the nitrosonium intramolecular mode in $^{14}NO^+$ and $^{15}NO^+$ β-alumina. In this standard Raman scattering notation, *c* labels the optic axis while *a* and *a'* lie in the plane perpendicular to the *c* axis although not necessarily corresponding to the crystallographic axes. The frequency of the $^{14}NO^+$ intramolecular mode is 2248 cm^{-1}, while the $^{15}NO^+$ intramolecular mode has a frequency of 2210 cm^{-1}, resulting in an isotopic shift of 38 cm^{-1}.

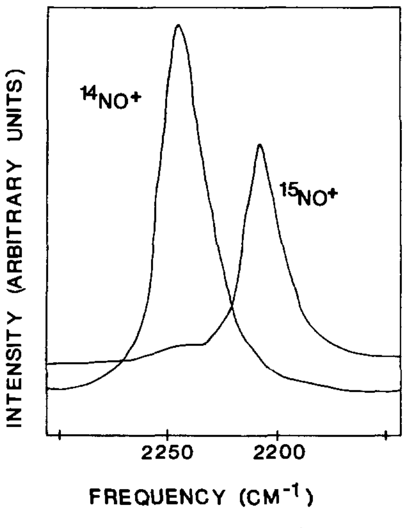

FIG. 1. Raman scattering spectra of the intramolecular stretching mode in NO^+ β-alumina in an *a*(*cc*)*a'* scattering geometry comparing the isotopic shift between $^{14}NO^+$ and $^{15}NO^+$. Full-scale intensity for the $^{14}NO^+$ spectrum is 20,000 counts/sec and for the $^{15}NO^+$ spectrum is 10,000 counts/sec.

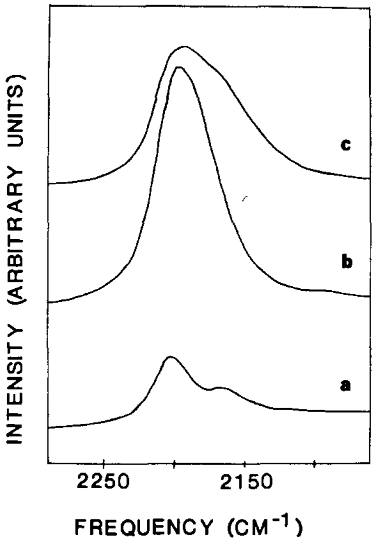

FIG. 2. Raman scattering spectra of the intramolecular stretching mode in NO^+ β''-alumina in an *a*(*cc*)*a'* scattering geometry comparing the isotopic shift between $^{14}NO^+$ and $^{15}NO^+$. Full-scale intensity of spectrum a is 10,000 counts/sec and for spectra b and c is 100,000 counts/sec. Spectra a and c are mixed $^{14}NO^+$ and $^{15}NO^+$ β''-alumina while spectrum b is $^{14}NO^+$ β''-alumina.

The frequencies of the nitrosonium intramolecular mode in $^{14}NO^+$ and $^{15}NO^+$ β''-alumina can be compared in the *a*(*cc*)*a'* experiment shown by spectrum a in Fig. 2. The $^{14}NO^+$ intramolecular mode frequency is 2203 cm^{-1} and the frequency of the $^{15}NO^+$ intramolecular mode is 2167 cm^{-1}, resulting in an isotopic shift of 36 cm^{-1}. Spectrum a of Fig. 2 was measured in a sample of β''-alumina that was obtained from a different melt than the previous samples of β''-alumina. The frequency of the $^{14}NO^+$ intramolecular mode is shifted 10 cm^{-1} higher than the observed value for the same mode in the previous β''-alumina samples. Raman spectra measured from additional samples obtained from the same melt showed the data to be reproducible.

Spectra b and c of Fig. 2 compare the $^{14}NO^+$ intramolecular mode with the intramolecular modes observed in a sample with both $^{14}NO^+$ and $^{15}NO^+$ present. Only one broad asymmetric mode is observed for the sample containing both $^{14}NO^+$ and $^{15}NO^+$. Spectra b and c were measured in samples of β''-alumina grown from the same melt.

Data Analysis and Discussion

The equations from which the harmonic frequency and the cubic anharmonic force constant were determined can be derived from expressions found in almost any text containing an advanced discussion of vibrational spectroscopy (*3*).

The fundamental transition frequency of a diatomic molecule (or ion) containing isotopic species i is $\omega_i = \omega_{ei} - 2\omega_e x_{ei}$ where ω_{ei} is the harmonic frequency and $-2\omega_e x_{ei}$ is the cubic anharmonic force constant. By identifying the subscript 1 with $^{14}NO^+$ and subscript 2 with $^{15}NO^+$, it is easy to show that

$$\omega_{e1} = \frac{\dfrac{\mu_1}{\mu_2}\,\omega_1 - \omega_2}{\left[\dfrac{\mu_1}{\mu_2} - \left(\dfrac{\mu_1}{\mu_2}\right)^{1/2}\right]} \tag{1}$$

and

$$-2(\omega_e x_{e1}) = \frac{\omega_2 - \omega_1\left(\dfrac{\mu_1}{\mu_2}\right)^{1/2}}{\left[\dfrac{\mu_1}{\mu_2} - \left(\dfrac{\mu_1}{\mu_2}\right)^{1/2}\right]} \tag{2}$$

Since ω_1 and ω_2, the fundamental transition frequencies, are measured directly from the spectra of the nitrosonium intramolecular mode for both $^{14}NO^+$ and $^{15}NO^+$ in each material, the harmonic frequency and the cubic anharmonic force constant for the $^{14}NO^+$ intramolecular mode can be calculated in both β- and β''-alumina and compared.

The harmonic frequency of the $^{14}NO^+$ intramolecular mode in β-alumina was found to be 2375 cm^{-1} and a cubic anharmonic force constant of -127 cm^{-1} was calculated. The $^{14}NO^+$ intramolecular mode in β''-alumina was determined to have a harmonic frequency of 2398 cm^{-1} and a cubic anharmonic force constant of -195 cm^{-1}. The error in these values is estimated by standard methods to be about 1.5 times the error in a single measurement of the frequency, which in this study was about ± 3 cm^{-1} due to the breadth of the bands. Therefore, the calculated uncertainty in both the harmonic frequency and anharmonic force constant is considerably smaller than the differences in those quantities found between β- and β''-alumina.

In the previous comparative spectroscopic study of NO$^+$ β and β'' alumina (*1*) the larger bandwidth of the intramolecular mode in the β'' crystal was attributed to a possible positional disorder induced by the repulsion between the nitrosonium ion oxygen atom and the O(3) oxygen atom of the spinel block. If the NO$^+$ ion occupies the 6*c* sites in β''-alumina, then in the perfect structure the intermolecular axis of NO$^+$ is directly in line with an O(3) atom above (below) the conduction plane and the center of the equilateral triangle formed by the three O(1) atoms below (above) the plane (*4*). However, the oxygen–oxygen repulsive forces described above would tend to prevent the NO$^+$ ion from assuming this position. Instead, the NO$^+$ ion may be expected to assume any of several equivalent orientations in which the internuclear axis is no longer parallel to the crystallographic *c* axis. This is unlike the case in β-alumina where the internuclear axis would point to the center of an equilateral triangle whose apexes are defined by spinel block oxygen atoms (*5*) both above and below the conduction plane. Therefore the larger cubic anharmonic stretching force constant of NO^+ in the β'' system as compared with the β system may be interpreted as reflecting greater positional disorder in the conduction plane. It should be emphasized that this positional disorder results from the unique nature of the interaction of the nitrosonium ion with the spinel block. However tempting it may be to identify the larger anharmonicity in β'' with the increased ease of gross ionic motion and higher ionic conductivity than in the β system (*6*), this identification would be erroneous since the normal mode being studied is an intramolecular mode and has little or no relationship to the motion of the ion as a whole except through indirect anharmonic coupling.

The difference between the observed frequencies of the nitrosonium intramolecular mode in the two different samples of β''-alumina is noteworthy. This results either from incomplete cation replacement in the conduction plane or may indicate that samples of β''-alumina obtained from two different melts are not perfectly identical.

Conclusions

The shape of the NO^+ intramolecular mode vibrational potential energy curve has been investigated in the vicinity of the minimum through the spectroscopic study of ^{15}N isotopically enriched crystals. The differences found in the harmonic frequency and cubic anharmonic force constant of the intramolecular mode were attributed to structural differences in the conduction planes of β- and β''-alumina. The larger value of the cubic force constant in the β'' system was consistent with a previous observation in which the bandwidth of the stretching mode was compared in the two aluminas.

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