Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **11**: 389–396, 1991.

Clathrate and Inclusion Compounds. Part 11 [1]. A pre-Resonance Raman Study of the β-Quinol/SO_2 Clathrate.

J. ERIC D. DAVIES* and VIVIENNE A. TABNER
Department of Chemistry, Lancaster University, Lancaster, Lancs., LA1 4YA, UK.

(Received: 15 May 1991; in final form: 5 August 1991)

Abstract. A pre-resonance Raman study of the yellow β-quinol/SO_2 clathrate has been carried out using 609.8, 586.8, 514.5, 488.0 and 457.9 nm excitation. Pre-resonance enhancement is observed for the guest ν_1 (A_1) band at 1147 cm^{-1} and the host band at 1257 cm^{-1}. These observations are consistent with a charge transfer interaction arising from the LUMO of SO_2 (S $3p_z$) and the HOMO of quinol, which consists mainly of the ring π electrons.

Key words. Clathrate, quinol/SO_2 clathrate, Raman spectroscopy, pre-resonance Raman effect.

1. Introduction

The clathrate formed between the β polymorph of quinol [$C_6H_4(OH)_2$] and SO_2 is very unusual in that it is one of the few coloured quinol clathrates, and thus lends itself to a resonance Raman study. The objective of the present work is to investigate whether such a study can provide information about the nature of the host-guest interaction giving rise to the yellow colour.

A previous resonance Raman study has been reported for this clathrate [2], using the 457.9, 488.0, 514.5 and 647.1 nm excitation wavelengths. Sodium sulphate was used as the internal intensity standard, but some of the nine Raman bands arising from the Na_2SO_4 (V) polymorph [3] overlapped with β-quinol bands and with the ν_1 (A_1) band of guest SO_2. This overlap reduced the number of host bands which could be examined and the resonance behaviour of the guest band could not be observed. Furthermore the band intensities were not corrected for the wavelength dependent response of the photomultiplier.

In view of these deficiences of the previous study we have re-examined the resonance Raman behaviour of the β-quinol/SO_2 clathrate, correcting the spectra for the varying photomultiplier response and using $NaNO_3$ as the intensity standard. Solid $NaNO_3$ gives three Raman bands at 724 cm^{-1}, $\nu_4(E')$, 1063 cm^{-1}, $\nu_1(A_1')$, and 1385 cm^{-1}, $\nu_3(E')$ which do not overlap with any of the host or guest bands. The use of this

---

* Author for correspondence at the Environmental Science Division, Lancaster University.

standard thus enables us to examine the behaviour of both the host *and* guest bands and provides us with the possibility of obtaining complete information on the host-guest interaction.

2. Experimental

A range of SO_2 clathrates with cage occupancies varying from 16% to 60% was prepared by bubbling SO_2 through a saturated solution of α-quinol in absolute ethanol at various temperatures. The methanol clathrate was prepared by recrystallising α-quinol from methanol. The samples were analysed using a thermogravimetric method. β-Quinol was prepared by slow recrystallisation of α-quinol from *n*-propanol [4]. $C_6H_4(OD)_2$ was prepared by recrystallising quinol from D_2O.

The Raman spectra were excited using visible radiation from Coherent Model 52 and Spectra Physics Model 164 argon ion lasers (457.9, 488.0 and 514.5 nm), and a Coherent Model 590 dye laser pumped by the Ar 514.5 nm line (586.8 and 609.8 nm). The spectra were recorded on a Cary 81 Raman spectrometer modified for 90 degree viewing and coupled to an Apple IIe micro computer [5]. The spectral response of the spectrometer system was calibrated using a National Physical Laboratories MJ5 standard lamp operated at 11V.

The sample consisted of a finely ground (< 125 μm) mixture of the clathrate and $NaNO_3$, contained in a spinning glass cell. The homogeneity of the mixture was tested by repeated scanning of the sample after removal from the spectrometer and shaking.

Ultraviolet excitation of Raman spectra was carried out at the Rutherford Appleton Laboratory using the 351.1 nm line from a Coherent Innova 90 cw argon ion laser, and the 360 nm line from a Lambda Physik FL3002 dye laser (DMQ dye) pumped by a Lumonics Hyperex 400 XeCl pulsed excimer laser operating at 308 nm. The spectra were recorded using a Spex Triplemate spectrometer and an OSMA diode array detector.

UV/visible absorption spectra of solid samples were recorded on a Pye Unicam SP-1800 spectrophotometer using barium sulphate as the reference.

3. Results and Discussion

Figure 1 shows that the uv/visible absorption spectra (200-700 nm) of β-quinol and of the methanol clathrate are very similar, but the spectrum of the SO_2 clathrate displays an additional band with a λ_{max} value of ~ 360 nm.

Pre-resonance studies were carried out on four samples with occupancies ranging from 16% to 60%. All samples showed similar behaviour which will be illustrated using the results obtained from the 56% occupancy sample.

The Raman spectra of a 56% cage occupancy SO_2 clathrate excited using different laser wavelengths are compared in Figure 2. It is apparent that the two bands at 1147 and 1257 cm^{-1}, marked *, increase in intensity relative to the most intense band at 1063 cm^{-1}, the $\nu_1(A_1')$ reference band of NO_3^-. The pre-resonance enhancement of these two bands is confirmed from the excitation profiles, based on peak areas, of a wide range of bands (Figure 3).

Attempts to obtain resonance Raman spectra of the SO_2 clathrate using 360 and 351.1 nm excitation were unsuccessful due to the decomposition of the solid sample despite using a spinning sample cell, diluting the sample with $NaNO_3$ or KBr and using varying laser power or pulse energy.

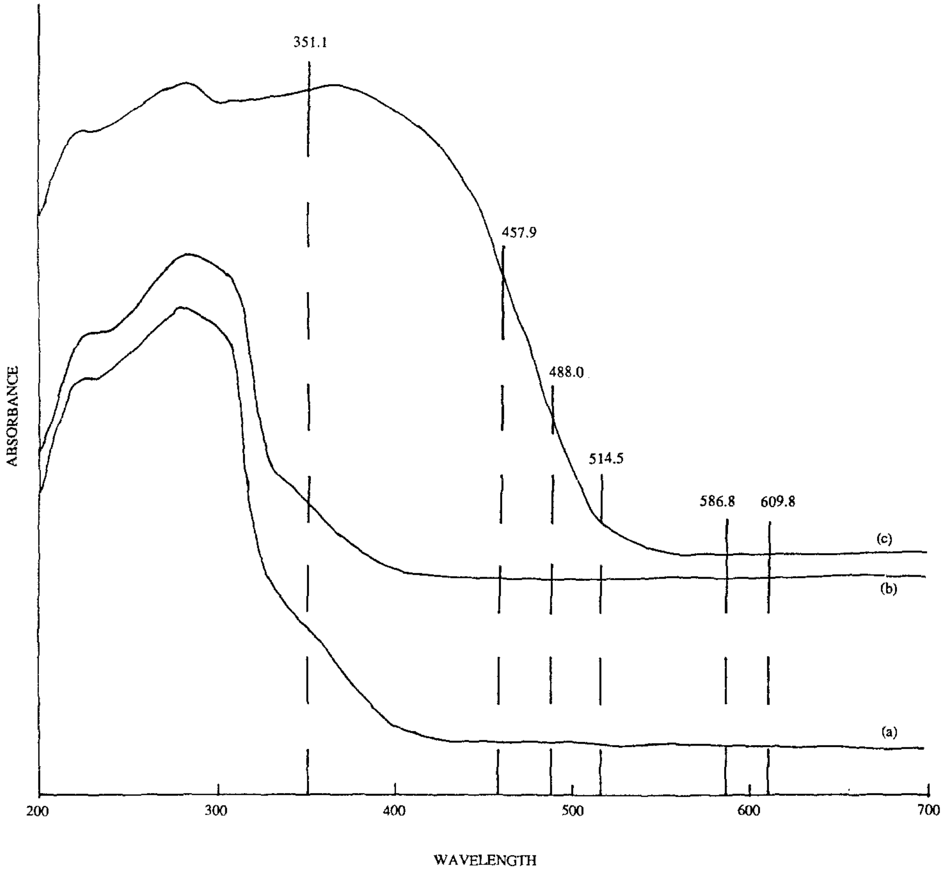

Fig. 1. The solid state uv/visible absorption spectra (200 - 700 nm) of (a) β-quinol (b) the methanol and (c) the SO_2 clathrate (56% cage occupancy).

The resonance behaviour of the SO_2 clathrate was compared with that of the white methanol clathrate.The bands arising from the methanol guest molecule were too weak to give accurate measurements, but the excitation profiles of the host bands (Figure 4) again show a pre-resonance enhancement of the quinol 1257 cm^{-1} band.β-Quinol itself also shows a pre-resonance enhancement of this band, but uv excitation (351.1 nm) shows a greater enhancement in the methanol clathrate than in the empty β-quinol lattice (Figure 5).

The above results suggest that the host-guest interaction involves that part of the host whose vibration gives rise to the Raman band at 1257 cm^{-1}. Suggestions have been made for the assignment of the infrared [6] and Raman [7] bands, but it is still incomplete. An attempt was made to clarify the assignment using the AM1 and MNDO programs [8]. Due to the tendency of these programs to over-estimate the wavenumber values it is still difficult to decide whether the 1257 cm^{-1} band arises from a bending mode of the quinol $(OH)_6$ hexameric unit or from a CH in-plane bending vibration of the benzene ring.

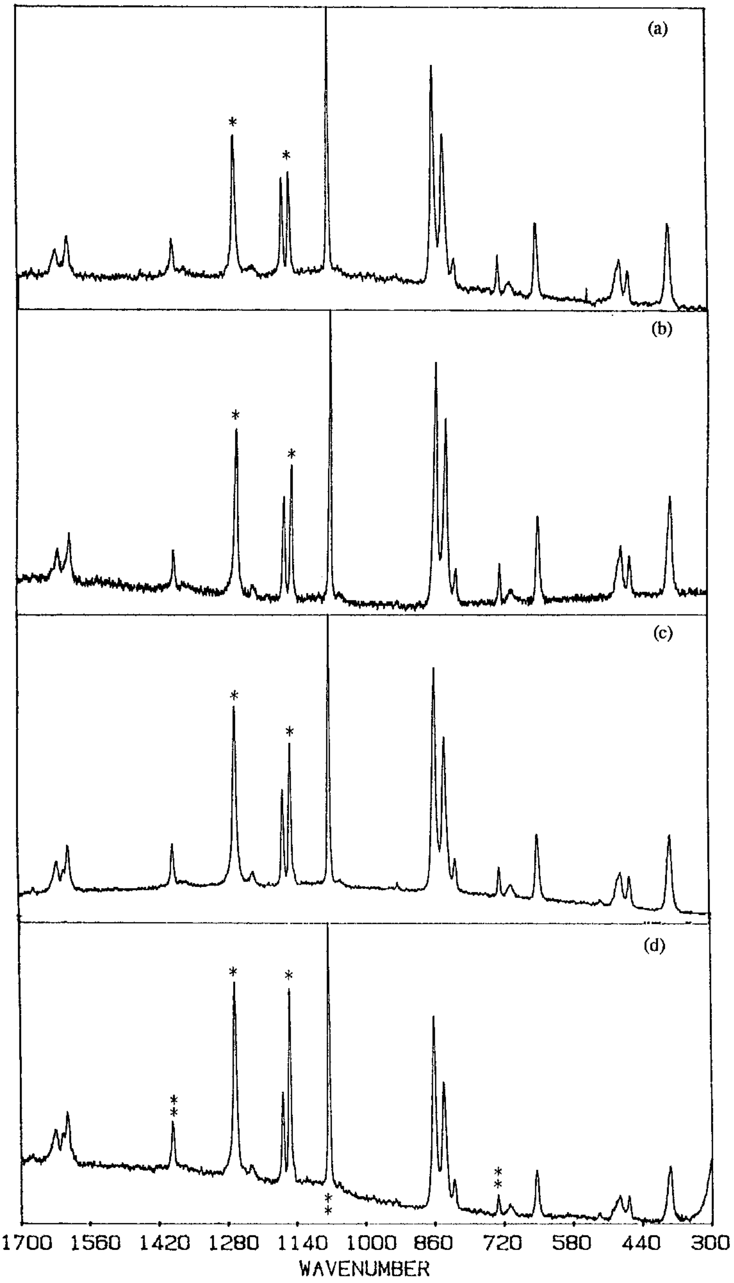

Fig. 2. Raman spectra of a 56% cage occupancy quinol/SO_2 clathrate excited using (a) 609.8 (b) 586.8 (c) 514.5 and (d) 457.9 nm. * indicates the bands displaying a pre-resonance enhancement. ** identifies the $NaNO_3$ bands in Fig. 2d.

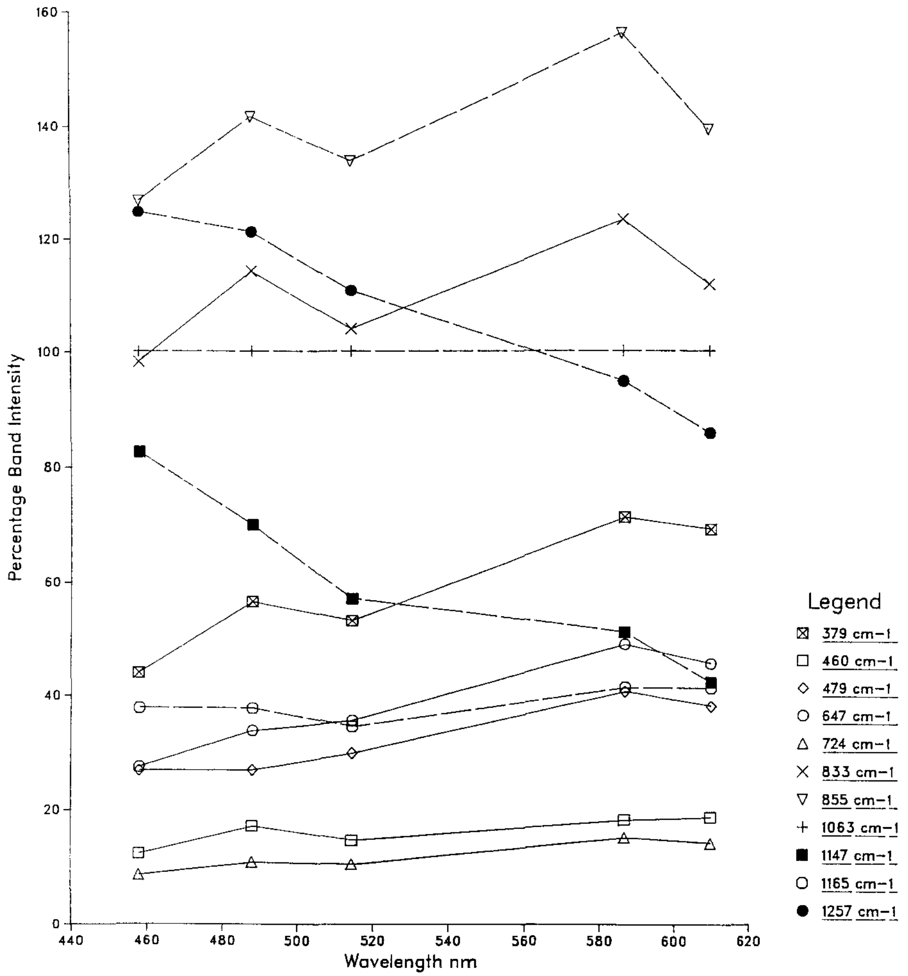

Fig. 3. Laser excitation profiles, based on peak areas, for the 56% cage occupancy quinol/SO_2 clathrate.

Some support for the assignment of the band to a vibration of the benzene ring can be obtained by comparing the Raman spectra of $C_6H_4(OH)_2$ and $C_6H_4(OD)_2$.

The Raman spectrum of α-$C_6H_4(OH)_2$ in the 1200-1300 cm^{-1} region consists of a broad asymmetric band centred at ~ 1259 cm^{-1} [9]. Deuteration causes the band to sharpen up considerably and become centred at 1257 cm^{-1} . Since the 1257 cm^{-1} component of the broad band is unaffected by deuteration, it is acceptable to assign it to the CH in-plane bending mode of the benzene ring rather than to a vibration of the $(OH)_6$ hexameric unit.

Crystallographic [10] and theoretical [11] studies also shed some light on this problem.Theoretical studies on the phenol/SO_2 charge transfer complex indicated the decisive interaction to be that between the LUMO of SO_2 (S $3p_z$) and the HOMO of phenol, which consists mainly of the ring π electrons, rather than that between the lone pair on the hydroxyl oxygen atom and the SO_2 LUMO [10]. It was suggested that a similar interaction could exist in the β-quinol/SO_2 clathrate.

Crystallographic studies [9] indicate that such an interaction is possible since the separation between the sulphur atom and one of the ring carbon atoms is 3.50 Å (*cf* with 3.55 Å for a van der Waals interaction). It is interesting to note that a weak interaction also exists between the oxygen atom of SO_2 and the $(OH)_6$ ring of the quinol framework with a smallest separation of 2.43 Å (*cf* with 2.45 Å for a van der Waals interaction).

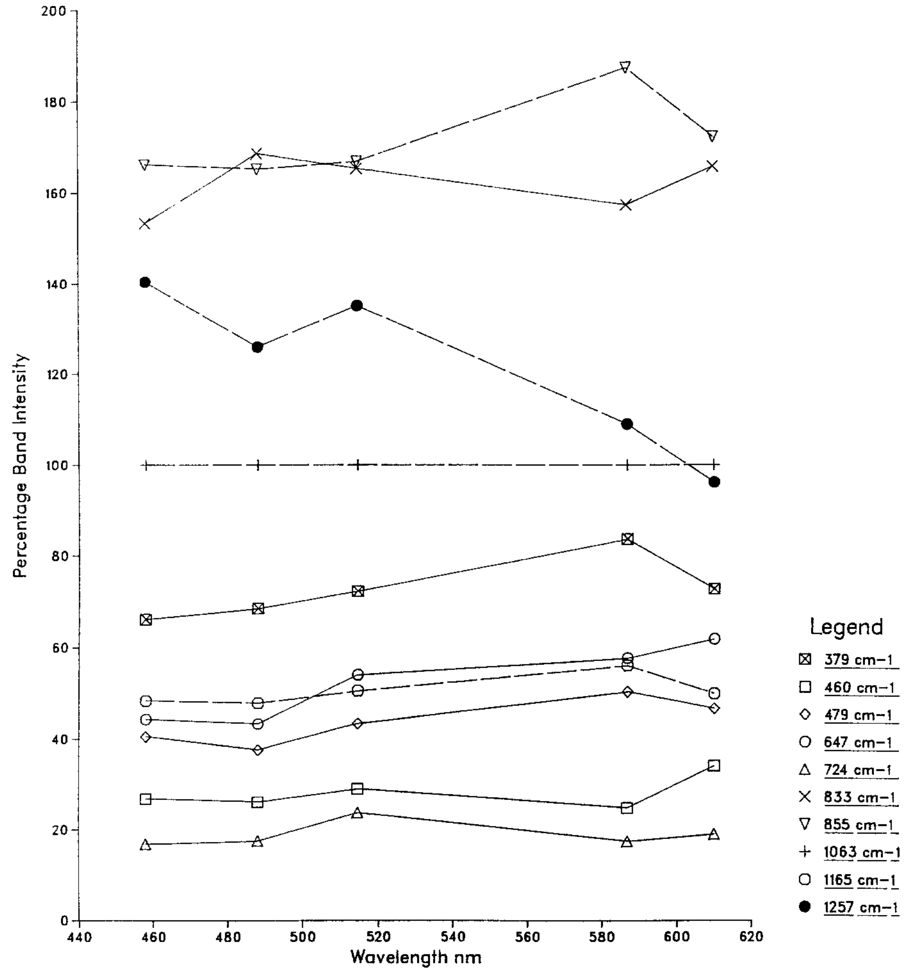

Fig. 4. Laser excitation profiles, based on peak areas, for the 98% cage occupancy quinol/methanol clathrate.

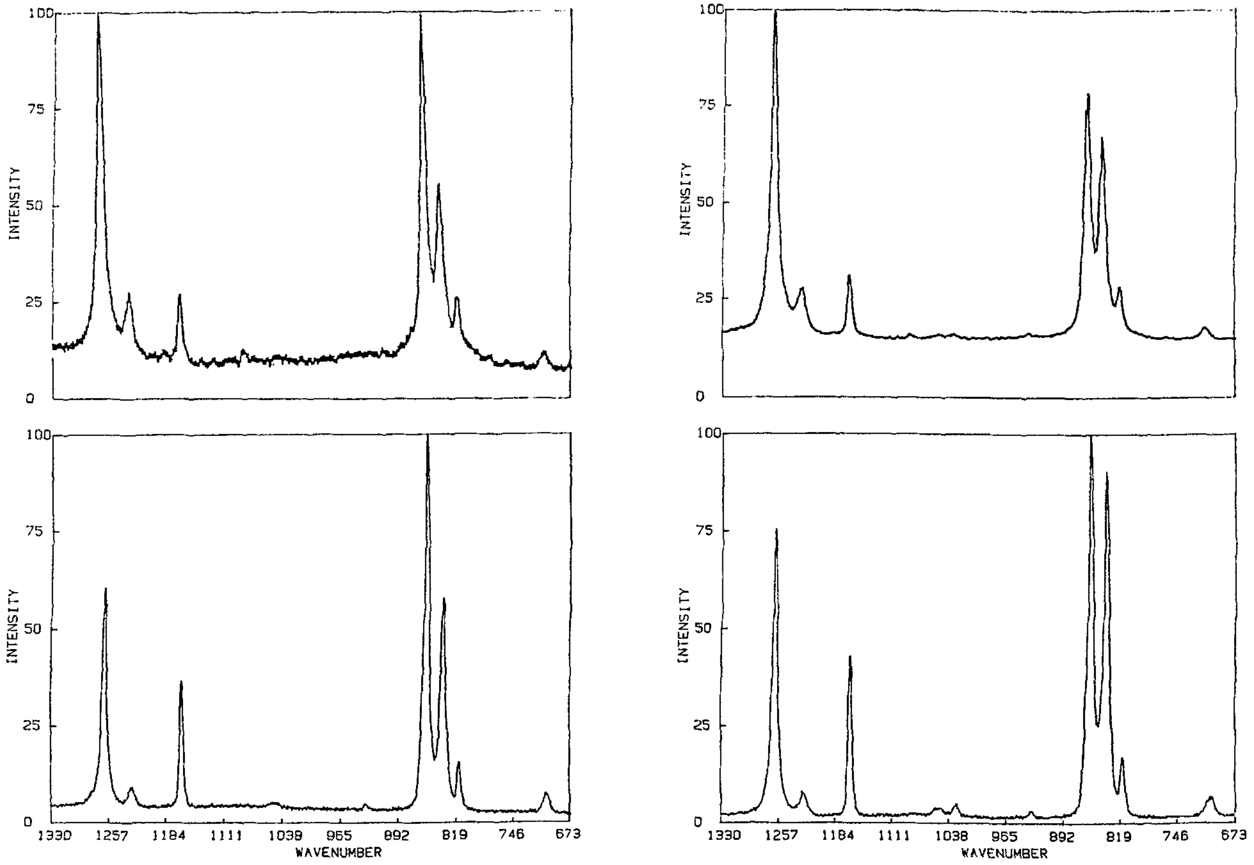

Fig. 5. The Raman spectra of β-quinol (left) and the quinol/methanol clathrate (right) excited using 514.5(lower) and 351.1 nm (upper) excitation.

4. Conclusions

The ability to observe the pre-resonance Raman behaviour of *both* the host *and* guest bands has shown an enhancement of the guest SO_2 band at 1147 cm^{-1} arising from the ν_1 (A_1) symmetric stretching mode and the host band at 1257 cm^{-1}, arising from a CH in-plane bending vibration of the benzene ring. These observations are consistent with the charge transfer interaction arising from the LUMO of SO_2 (S $3p_z$) and the HOMO of quinol which consists mainly of the ring π electrons.

Acknowledgement

We thank the SERC for a studentship (VAT) and for the use of the equipment at the Central Laser Facility of the Rutherford Appleton Laboratory.

References

1. Part 10. J.E.D. Davies and V.A. Knott: *J. Mol. Struct.* **174**, 229 (1988).
2. P.S. Santos and P.C. Isolani: *Chem. Phys. Lett.* **67**, 487 (1979).
3. J.E.D. Davies and W.F. Sandford: *J. Chem. Soc., Dalton Trans.* 1912 (1975).
4. D.F. Evans and R.E. Richards: *J. Chem. Soc.*, 3932 (1952).
5. J.E.D. Davies: *Comp. Enhanc. Spectrosc.* **3**, 73 (1986).
6. R.J. Jakobsen and E.J. Brewer: *Appl. Spectrosc.* **16**, 32 (1962).
7. M. Kubinyi and G. Keresztury: *Spectrochim. Acta* **45A**, 421 (1989).
8. J.E.D. Davies, J.T. Gleghorn, and V.A. Tabner: unpublished results.
9. J.E.D. Davies: *J. Chem. Soc., Dalton Trans.* 1182 (1972).
10. D.E. Palin and H.M. Powell: *J. Chem. Soc.* 208 (1947); T.M. Polyanskaya, V.I. Alekseev, V.V. Bakakin, and G.N. Chekova: *J. Struct. Chem.* **23**, 101 (1982).
11. J.S. Tse and J.A. Ripmeester: *J. Phys. Chem.* **87**, 1708 (1983).